THE CATALYTIC OXIDATION OF PERFLUOROPROPENE

By

WARNER HOWARD CHRISTIE

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CHAPTER I

INTRODUCTION

The phenomenon of catalysis was first observed and recorded in 1835, by J. J. Brezelius[1] who introduced the term catalytic agent into chemistry to include those substances which, by their mere presence and without being altered themselves, accelerate the rate of reactions. In reversible systems the catalyst accelerates the establishment of equilibrium until at the equilibrium point both foreward and reverse reactions are equally accelerated. It is possible to distinguish between homogeneous and heterogeneous catalytic reactions. The former generally occur in gases and liquids where the catalyst is dissolved, and the latter take place at gas-liquid, gas-solid or liquid-solid interfaces, the catalyst usually being the liquid or solid.

The theoretical chemist has attempted to understand the phenomenon of catalysis by way of the kinetic approach. This approach has not proved altogether satisfactory. Basically, the method of chemical kinetics involves the quantitative determination of the reaction products and their dependence on time and temperature and the expression of

rates in terms of concentrations and temperatures. A model or mechanism is then constructed to fit the observations. Such a mechanism has to include assumptions regarding the step or steps involved in the catalysis proper. A mechanism deduced in this fashion is generally considered correct until more or better measurements prove it wrong. It is not surprising that mistakes are made in interpreting kinetic data when it is considered that at least five steps[2] are involved in a heterogeneous catalytic reaction. These are the diffusion of the reacting molecules to the surface, the adsorption of the gases on the surface, reaction on the surface, desorption of the products and finally the diffusion of the desorbed products into the main body of the gas stream.

The slowest of these steps will determine the rate of the over-all reaction. In many cases wrong conclusions have been drawn as to which step is actually rate determining in a given reaction. It is no surprise, therefore, that the mechanism of the rearrangement of molecules on a surface cannot be deduced from kinetic measurements alone. A systematic approach would use kinetic data to supplement more direct physical measurements and observations concerning the surface involved.

Recently, investigators have shifted their attention from the reactants and products to a detailed consideration

of the structure and properties of the solid catalyst itself. The techniques and theories of solid state physics have now been successfully applied to a number of solid catalysts. Consequently, at this time, the electronic nature of the solid has become a factor of major interest to workers[3,4] in this field.

The catalyst unit may be thought of as a group of near neighbor atoms whose configuration or properties are such that they exert the required forces on the reactant to assist in breaking some bonds and forming other bonds. Proper orientation of the reactants is required on the surface so that the atoms needed for formation of products are in close proximity. The lattice spacing or the geometry of the surface of a solid and the unsaturated valence forces determine the forces of attraction of different catalyst atoms for the various parts of the reactant molecules. As such forces only operate over short distances, the interaction is largely determined by the relative spacing of surface and reactant atoms. The discovery of fivefold differences in the intrinsic catalytic activity of oriented and non-oriented films of the same metal proves conclusively the importance of the catalyst lattice parameter in catalysis.[5]

The purpose of this investigation was to attempt to find materials which would serve as catalysts for the reactions of fluorocarbons. Saturated flurocarbons are

known to possess great chemical and thermal stability. These properties make fluorocarbons extremely valuable in certain applications but also make it impossible to apply the classical synthesis or degradation methods used in organic chemistry.

Fluorocarbons as a field of chemical substances were only first reported in 1937. In that year and more extensively in 1939 the preparation and properties of liquid fluorocarbons were disclosed by Simons and Block.[6,7] Because of certain desirable properties, fluorocarbons were in demand during World War II. The science and technology of fluorocarbons was still in its infancy and the impetus of war spurred many developments in the field. Several methods were devised for the production of fluorocarbons. A modification of the catalytic vapor-phase fluorination technique introduced by Fredenhagen and Cadenbach[8] and by Bigelow and co-workers[9-12] was developed at Columbia University. At the same time the metallic fluoride process[13] was being perfected at the Johns Hopkins University. In this same period still another method was invented by Simons.[14] This was the electrochemical process the announcement of which appeared in 1949. The Simons method has proved to be the most versatile for the production of fluorocarbons.

Since the science of fluorine chemistry is relatively new, few guiding principles were available for the selection of materials to be used as catalysts. The approach used

in this work is one familiar to those working in catalysis. Substances that could be conceived of as possible catalysts were simply tested, in an experiment, to determine whether or not they were suitable.

The reaction of $CF_3CF{=}CF_2$ with oxygen was investigated because this system offered a definite possibility for formation of useful products. Fluorocarbon olefins are known to be reactive. The simultaneous oxidation and hydrolysis of olefins containing a perfluoro-alkyl group has been used for the preparation of acids.[15]

$$3CF_3CCl{=}CCl_2 + 4KMnO_4 + 14KOH =$$

$$3CF_3CO_2K + 4MnO_2 + 3K_2CO_3 + 7H_2O + 9KCl.$$

In a similar fashion the oxidation of $(CF_3)_2C{=}CF_2$ produces hexafluoroacetone in good yield.[16] Highly unsaturated perfluoro-olefins such as $CF_2{=}CF\text{-}CF{=}CF_2$ are reported to undergo oxidation[17] in air or oxygen. Swarts has reported the oxidation[18] of $CFBr{=}CF_2$. The combustion of $CF_2{=}CF_2$ in oxygen is reported by Benning and Parks[19] to result in the formation of CF_4, although, in general, acid halides appear to be the principal products formed by the air oxidation of perhalo-olefins. Hurka prepared $CClF_2COF$ in good yield by oxidizing[20] $CClF{=}CF_2$ with oxygen in the absence of a catalyst in an autoclave at 100-300 lb. per sq. in.

Myers[21] reported the formation of a peroxide in the oxidation of $CClF{=}CF_2$ with O_2. These experiments were

performed at room temperature, at autogenous pressures, and in the absence of light. The peroxide formed was never isolated in the free state.

A number of attempts at oxidizing $CF_3CF{=}CF_2$ over some of the classical catalysts of organic chemistry failed to give satisfactory results. Work done by Gens and Wethington suggested that alkali fluorides might serve as catalysts for this reaction. In a recent paper[22] these workers demonstrated that certain fluorocarbon compounds, $CF_3CF{=}CF_2$ in particular, exchanged fluorine atoms rapidly with the alkali fluorides. The order of exchange was reported to be Cs $>$ Rb $>$ K, Na, Li.

The work done in this research is divided into two phases. The first phase is entitled "Preliminary Experiments," and in this section there are described the various experiments performed in the search for materials that would function as catalysts for the oxidation of $CF_3CF{=}CF_2$. The second phase is entitled "Comparison Experiments." In this section a set of experiments is described in which various surfaces are evaluated, in a quantitative fashion, for ability to catalyze the oxidation of $CF_3CF{=}CF_2$.

CHAPTER II

APPARATUS

Apparatus Used in the Preliminary Experiments

A reactor tube was fabricated from a 33 cm. length of 2.14 cm. I.D. nickel tubing. The ends of this tube were closed by attaching nickel plugs with silver solder. Each plug had a 3/8 in. outlet hole onto which a 15 cm. length of 3/8 in. nickel tubing was flush silver soldered. A second reactor tube, 15 cm. in length, was constructed in the same fashion.

The reactor temperature was controlled by a Simplytrol pyrometer unit which automatically turned the furnace unit off and on to maintain, within $\pm 5^{\circ}$, the preselected temperature. An iron-constantan thermocouple, silver soldered to the center portion of the reactor, actuated the pyrometer unit. The reactor was heated by a clam type tube furnace.

The gaseous materials to be reacted were passed through the reactor in either of two ways. First, the materials were taken directly from the storage cylinders and were metered into the reaction system in the desired ratio.

Secondly, the materials were mixed in the desired ratio in a 27 l. glass container and were then displaced by water, at some given rate, into the reaction system.

Before entering the reaction system, the wet gases passed through two drying tubes. The first tube which contained Drierite was 90 cm. in length and 2 cm. in diameter. The second tube which contained P_2O_5 was 40 cm. in length and 2 cm. in diameter. The reaction products were collected in a suitable series of cold traps. The end trap was protected from moisture by a drying tube.

Apparatus Used in the Comparison Experiments

Individual reactors were fabricated for each catalyst studied in the comparison experiments. These reactors were constructed in the same fashion as those used in the preliminary experiments. The reactor dimensions were: length, 15 cm.; I.D., 2.14 cm.; with outlet tubes 25 cm. long. Iron-constantan thermocouples were silver soldered to the center of each reactor tube. This thermocouple was connected to a potentiometer that was capable of reading 0.001 mv. The average temperature range observed with this potentiometer is the value reported in the tables in the comparison experiments. Temperature control was maintained by a Simplytrol pyrometer. The controlling thermocouple was placed in a nickel well of 7.0 cm. length, and 0.3 cm. I.D., which was attached to the center part of the reactor tube

by wrapping with asbestos tape. The entire reactor tube was then insulated by wrapping it with several layers of asbestos tape. The pyrometer unit operated the furnace through a variable Powerstatt. The Powerstatt was operated at approximately 15 volts above that required to maintain the desired reactor temperature. This arrangement was found to be capable of holding any temperature up to 400° within ±1.5°.

A number of glass product traps were prepared with stopcocks on each outlet tube. These traps were used to collect and weigh the reaction products. Each trap was approximately 20 cm. in length by 2.5 cm. in diameter. The center outlet tube came within 3 cm. of the bottom of the trap. This provision was made so that all condensable gases would be pulled through the cold zone when the traps and products were being degassed.

A schematic diagram of the flow system used is shown in Fig. 1. The reactant gases were contained in a 27 l. water operated bottle, A. The feed material was metered through a needle valve, B, which was connected to a wet test meter, C. The water saturated reactants then passed through two drying tubes. The first drying tube, D, was 90 cm. in length by 2 cm. in diameter and contained indicating Drierite. The second drying tube, E, contained P_2O_5 and was 50 cm. in length by 4 cm. in diameter. These drying tubes were connected to a Fischer and Porter Flowrator, F, which

had been calibrated for the feed mixture used. This meter was connected to a three way stopcock, G, which connected to the reactor, H. The third opening on stopcock G was open to the atmosphere through two drying tubes, I and J. Upon completion of a run, dry nitrogen was swept through the reactor from stopcock G through drying tubes I and J.

The outlet of the reactor, H, was connected to another three way stopcock which could be opened to the atmosphere and the issuing gas stream checked with indicating paper to ascertain whether or not reaction was occurring. Stopcock K was connected to the product receiver, L, which was open to the atmosphere through a drying tube, M. All tubing connections were made with new, 3/8 in. Tygon tubing.

Distillation System

A distillation column was used to separate the products formed in the oxidation reactions. This column was of vapor take-off design and would handle materials boiling as low as -60°. For ease of maintenance, the column was made in three separate pieces each of which was fitted with standard taper joints. The head had a Dewar type container built in, which could be cooled with Dry Ice-acetone, to act as a condenser surface. The column tube was 45 cm. in length with an I.D. of 0.8 cm. and had a silvered vacuum jacket. This column was packed with 1/16 in. I.D. single-turn, stainless steel helices of No. 36 B and S gauge wire.

LEGEND FOR FIG. 1

A. Water Operated 27 l. Storage Battle

B. Needle Value

C. Wet Test Meter

D. Drierite Drying Tube

E. P_2O_5 Drying Tube

F. Flowrator

G. Three Way Stopcock

H. Nickel Reactor Tube

I. P_2O_5 Drying Tube

J. Silica-Gel Drying Tube

K. Three Way Stopcock

L. Product Receiver

M. Drying Tube

N. Nitrogen Tank

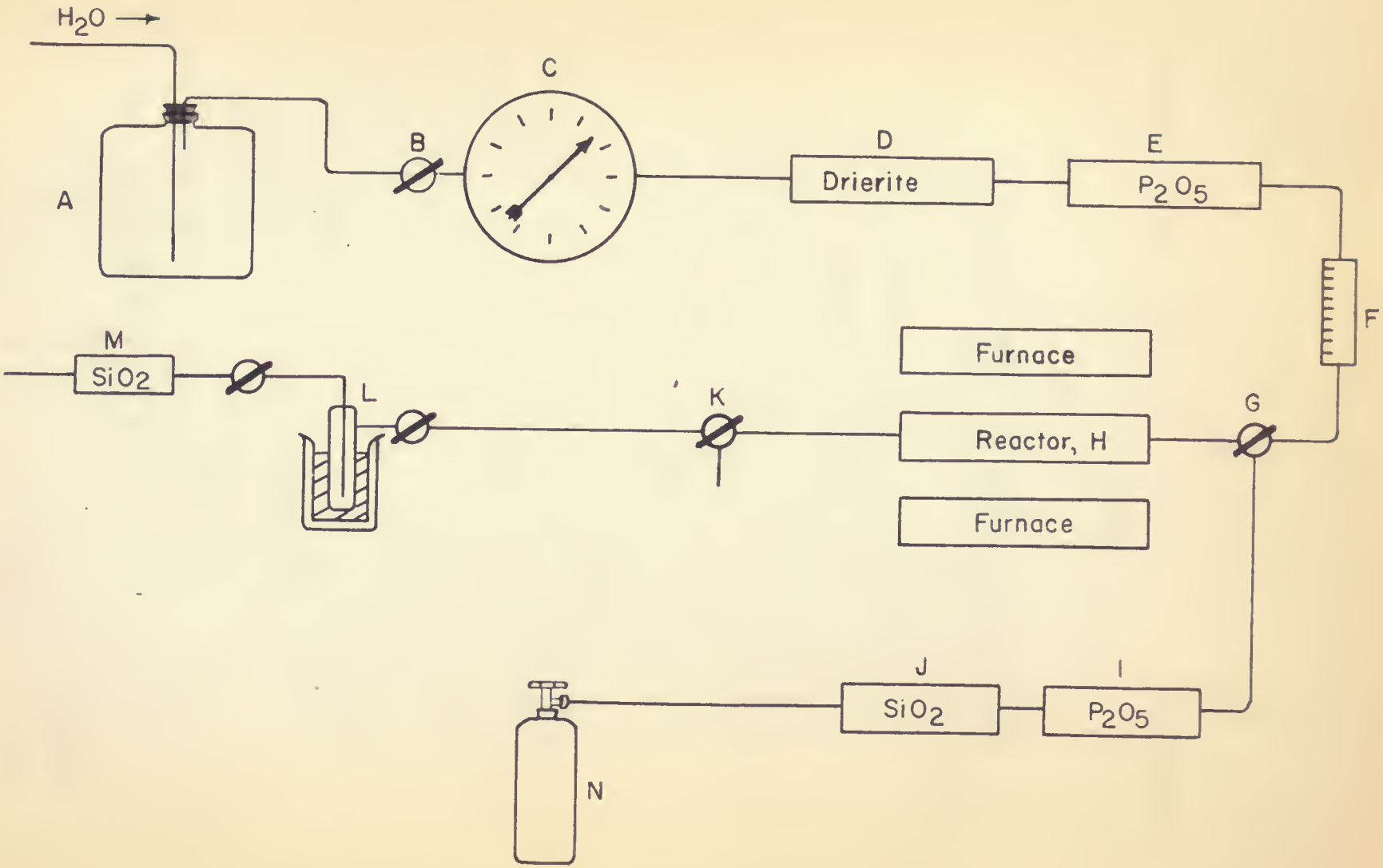


Fig. I, System Used in the Comporison Experiments

For hydrocarbons, this column was estimated to have the equivalent of 30 theoretical plates.[23] For fluorocarbons, it was believed that this value would be reduced somewhat. The distillation pots, of various sizes, were equipped with thermocouple wells and were constricted at the bottom to accomodate a heating coil.

The column head was permanently attached to an all glass vacuum system specially constructed for use with a distillation column. This vacuum system had a series of four traps to accommodate the various fractions of a distillation, a manometer to measure pressure, a P_2O_5 tube for drying, and an outlet for making Regnault[24] type molecular weight determinations.

Analytical System

An analytical system was devised to determine the percentage of COF_2 in the COF_2, CF_3COF mixture obtained in some of the preliminary experiments. This same apparatus was used to determine the percentage conversion values listed in the comparison experiments.

A 500 ml. filter flask was fitted with a wide mouth inlet tube, through a rubber stopper, that extended to within 1 cm. of the bottom. The external end of the inlet tube was equipped with a stopcock. The rubber stopper was also fitted with a separatory funnel. This apparatus was tested and found to be leak proof when assembled. A glass

enclosed iron stirring bar, which was operated by a powerful external magnet, was included in the flask. The side arm outlet on the filter flask was connected to a Drierite drying tube which was connected in series to a P_2O_5 drying tube. The P_2O_5 drying tube was in turn connected to a stopcock equipped product trap. In operation, enough 20 per cent NaOH solution was placed in a flask to cover the inlet tube with 2 to 3 cm. of solution. One pass through this solution, with vigorous stirring, was found to effectively remove all the acidic products. Carbonyl fluoride was determined by acidifying the basic solution and measuring the CO_2 evolved. This was accomplished by closing off the inlet tube stopcock and adding concentrated H_2SO_4 from the separatory funnel while stirring the solution.

CHAPTER III

CALCULATIONS AND MATERIALS

Calculations

The contact times reported in some preliminary experiments and in all the comparison experiments were calculated from the following equation:

$$C.\ T. = \frac{(Mr)\ \ (t)}{(Mt)}\ , \qquad (1)$$

where C. T. = average contact time,

Mt = moles of gas mixture passed through the reactor in time t,

Mr = moles of gas mixture contained in the reactor at the reaction temperature,

t = time required for Mt moles of gas mixture to have passed through the reactor.

Applying the ideal gas law, Mr and Mt were expanded to the following:

$$Mr = \frac{(P)\ \ (Vr)}{(R)\ \ (Tr)}$$

and $$Mt = \frac{(P)\ \ (V)}{(R)\ \ (T)}\ ,$$

where P = atmospheric pressure (assumed to be 760 m.m. for all experiments),

Vr = free volume of the packed reactor,

R = gas constant,

Tr = reaction temperature, ^{o}K,

V = gas volume passed in time t,

T = room temperature.

Substituting these expressions for Mr and Mt back into equation (1) gave equation (2):

$$C.\ T. = \frac{(Vr)\ (T)\ (t)}{(Tr)\ (V)} . \qquad (2)$$

The measured volume of gas mixture passed, Vm, required a correction for the water vapor removed by the drying tubes to give the true volume of gas mixture passed, V. This correction took the following form:

$$Vm = V + V_{H_2O}, \quad \text{where} \qquad (3)$$

V_{H_2O} = volume of water vapor removed.

Application of Boyle's law to the term V_{H_2O} gave the following relation:

$$V_{H_2O} = \frac{P_{H_2O,m.m.}}{760}\ (Vm), \quad \text{where} \qquad (4)$$

$P_{H_2O,m.m.}$ = vapor pressure of H_2O at room temperature.

Substitution of (4) into (3) and rearranging gave equation (5):

$$V = Vm - \frac{P_{H_2O,m.m.}}{760}\ (Vm). \qquad (5)$$

Substitution of (5) into (2) gave the final form of the contact time relation used for calculation:

$$C.\,T. = \frac{(Vr)\,(T)\,(t)}{Tr\left(Vm - \frac{P_{H_2O,m.m.}}{760}\,(Vm) \right)} \quad .$$

The term Vr was calculated from the following relation:

$$Vr = V_{E.R.} - Vc \ ,$$

where $V_{E.R.}$ = calculated volume of the empty reactor,

Vc = volume of catalyst in reactor.

The quantity Vc was evaluated by dividing the weight of catalyst charge by its density. No information was found in the literature concerning the variation of density of the solid alkali fluorides with temperature. To overcome this difficulty the following approximation was made. Density values reported in Gmelins Handbuch der anorganischen Chemie[25-29] were plotted versus temperature. Unfortunately these reported values fell into two classes, those determined at or near room temperature and those determined at or near the melting point of the salt. For each salt these points were connected with a straight line. The average density value for the temperature range of each set of experiments was determined from the graph for each alkali fluoride. This average density value was used to calculate Vc.

For the two Group II fluorides used the only reported density values found[30,31] were those at room temperature. Consequently these are the values that were used in the calculations of Vc. These values introduced a small error into the calculated contact times for the experiments with CaF_2 and BaF_2.

In a strict sense the term Mr should be replaced by an expression that accounts for the amount of reaction taking place that would change the number of moles of material in the reactor. Although this factor probably influences the contact time values at high percentage conversions, no attempt was made to correct for it. The error introduced by this effect would probably be smaller than the variation in the contact time.

Chemicals Used

Hopcalite oxidation catalyst was purchased from the Mine Safety Appliance Company. This catalyst is generally a mixture of MnO_2, CuO, Co_2O_3 and Ag_2O.[32] No analysis was available for this material. The product was supplied as a 14/20 mesh granular solid and was used directly in this form.

Cupric oxide, "Baker and Adamson" reagent grade, was supplied in wire form. No appreciable impurities were present. No treatment other than streaming with oxygen at 400° was performed on this oxide before using.

Lithium fluoride, "Baker Analyzed" reagent grade, was supplied as a fine powder. This material was unsatisfactory in this form since it produced an excessive pressure drop across the reactor. This condition was alleviated by preparing a mixture of the insoluble powder with water and taking the resulting slurry to dryness on a hot plate while stirring. After screening out the fine material and crushing the large lumps, the product obtained was found to be suitable for use in the reactor. The chief impurities in this fluoride were listed as K, 0.01% and Na, 0.07%.

Sodium fluoride, technical grade, was obtained from the Harshaw Chemical Company as 1/8 in. tablets. No analytical data was available for this material. Before these tablets were used, they were crushed and the fine particles were eliminated by screening.

Potassium fluoride, "Baker and Adamson" reagent grade, was supplied in granular form. The major impurities were listed as HF, 0.05% and K_2CO_3, 0.10%. This granular form was found suitable for use in the reactor without further treatment.

Rubidium fluoride, in finely powdered form, was obtained from the Oak Ridge National Laboratory. This powder was unsuitable for use in the reactor. To produce a coarse material, this fluoride was recrystallized from water in a platinum vessel by taking the solution to dryness on a hot plate. It was necessary to use platinum

vessels rather than glass as this fluoride is sufficiently hydrolyzed in aqueous solution to attack glass. This fluoride is also reported to be decomposed by CO_2 in aqueous solution to form HF which would attack glass. The chief impurities in this material were reported to be K, 1.03% and Cs, 0.16%.

Cesium fluoride was obtained from the A. D. Mackay Company. The reported impurities included 0.12% Rb. This powder was recrystallized from water, in a platinum vessel, to obtain a form more suitable for use in the reactor.

Barium fluoride, "Baker and Adamson" reagent grade, was used in the comparison experiments without further treatment.

"Baker and Adamson," reagent grade CaF_2 was obtained as a fine powder. This powder was slurried with water and taken to dryness on a hot plate to produce a product suitable for use in the reactor.

Perfluoropropene was prepared by the decarboxylation of $CF_3CF_2CF_2COONa$ according to the procedure of La Zerte.[33] This material was scrubbed twice through 20% NaOH to remove any CO_2 present. Molecular weight checks on the final product were always within 1% of the theoretical value.

The piperazine and N-phenylpiperazine derivatives of a number of perhalo-acids were prepared in the course of this research. The following perfluoro-acids, $CF_3(CF_2)_nCOOH$ (where n = 0,1,2,4 and 6) and $HOOC(CF_2)_3COOH$ were obtained

from the New Products Division of the Minnesota Mining and Manufacturing Company. The following perhalo-acids, $Cl(CF_2CFCl)_2\ CF_2COOH$ and $Cl(CF_2CFCl)_3COOH$ were obtained from the Chemical Manufacturing Division of the M. W. Kellogg Company. No analyses were specified for these acids which were used in the preparation of derivatives without further purification.

CHAPTER IV

PRELIMINARY EXPERIMENTS

Reference is occasionally made to low-boiling and high-boiling products. This usage indicates, respectively, that the material being discussed boils below or above the fluorocarbon starting material. All temperatures referred to in this manuscript are on the Centigrade scale unless otherwise stated.

Experiments over CuO and Hopcalite

Four preliminary experiments were performed with CuO. Quantitative data concerning product yields is lacking but useful qualitative deductions can be made from these runs. These experiments are best summarized in Table 1. A brief paragraph is included about each run in the following text.

Experiment 65 I: The reactants were metered separately into a 33 cm. reactor packed with 331 g. of CuO. The center part of this reactor was maintained at 506°. One hundred and nineteen grams of material were collected in the Dry Ice and liquid air-cooled product traps. By weight,

TABLE 1

REACTIONS OF $CF_3CF=CF_2$ OVER CuO AND HOPCALITE

Run No.	Reactor and Packing	Reactor Temp.	Mole Ratio $O_2/CF_3CF=CF_2$	Flow Rate cc./min. at Room Temp.	Moles of $CF_3CF=CF_2$			Products and Remarks
					Initial	Recovered	Used	
				Reactions Over CuO				
65 I	33 cm. Reactor 331 g. CuO	506°	0.10	28.2	0.71	0.25	0.46	65% by weight of material believed to be CO_2. 6.0 g. of neutral high boiling material. Trace of $CF_3C(OH)_2CF_3$.
89 I	33 cm. Reactor 342 g. CuO	400°	Olefin Only	6.3	0.35	0.31	0.04	Recovered 90.5% of starting material. Some CO_2 obtained.
93 I	Same as 89 I	450°	Olefin Only	8.1	0.24	0.17	0.07	Recovered 69% of starting material. 14% by weight CO_2 in products.
96 I	Same as 93 I	430°	0.50	9.9	0.40	0.14	0.26	Recovered 35% of starting material. Large amount of CO_2 formed. Reactor plugged by CuF_2 formation.

TABLE 1 - Continued

Run No.	Reactor and Packing	Reactor Temp.	Mole Ratio $O_2/CF_3CF=CF_2$	Flow Rate cc./min. at Room Temp.	Moles of $CF_3CF=CF_2$			Products and Remarks
					Initial	Recovered	Used	
				Reactions Over Hopcalite				
119 I	15 cm. Reactor 62 g. Hopcalite	300°	0.53	9.6	0.23	0.03	0.20	Obtained 87% conversion to CO_2. No other products found.
120 I	15 cm. Reactor 63 g. Hopcalite	200°	0.57	13.0	0.27	0.09	0.18	Obtained 35% conversion to CO_2. $CF_3C(OH)_2CF_3$ made in 3.5% yield.
122 I	15 cm. Reactor 61 g. Hopcalite	150-180°	0.98	23.0	0.34	0.26	0.08	Recovered 77% of olefin unreacted.

65% of these products were soluble in NaOH solution. Absence of fluoride ion in this solution indicated that this soluble material was CO_2. Six grams of material boiling above 0° was obtained. Chromatographic analysis indicated that seven components were present in this material. Approximately 0.5 g. of white, needle like crystals were obtained in the wet ice-cooled trap. This material was found to be $CF_3C(OH)_2CF_3$.

Experiment 89 I: The reactor used in the previous run was repacked with fresh CuO for this experiment. Pure olefin was passed through the reactor at 400°. On distillation, 90.5% of the starting material was recovered. A small trace of both low-boiling and high-boiling material was obtained. In view of these results the experiment was repeated at a higher temperature.

Experiment 93 I: The reactor used in experiment 89 I was used again without change in this run. Pure olefin was passed through the reactor at 450°. Upon distillation 69% of the starting material was recovered. Approximately 14% by weight of the products was CO_2. A trace of high-boiling material was obtained.

Experiment 96 I: The reactor used in the previous experiment was used unchanged in this run. Oxygen and $CF_3CF{=}CF_2$ were mixed in the 27 l. storage bottle in a one to two mole ratio. These gases were metered into the reactor at 430°. Distillation showed that 35% of the starting

material was unchanged. The material coming off overhead was taken up by $Ba(OH)_2$ solution. The precipitate thus obtained was completely soluble in dilute HNO_3 with the liberation of CO_2. This indicated the absence of material containing hydrolyzable fluorine. Upon completion of this run the CuO in the reactor was inspected. The formation of red CuF_2 explained the poor weight balances noted in these runs.

Results obtained in the oxidations over CuO were not satisfactory as the yield of useful products was very low. CuO appeared to be a reactant in this system rather than a catalyst.

Three preliminary experiments were performed with Hopcalite. This catalyst was found to be more active than CuO. These three experiments are tabulated in Table 1. The significant details, pertaining to each run, are discussed in the following paragraphs.

Experiment 119 I: The 15 cm. reactor was packed with 62.2 g. of commercial Hopcalite catalyst. Thirty-four grams (0.23 mole) of $CF_3CF{=}CF_2$ were mixed with 3.9 g. (0.13 mole) of oxygen gas in the water operated storage bottle. This material was passed through the reactor, held at 300°, at a rate of 9.6 cc. per min. Of a total of 38 g. of material passed, only 29 g. were recovered. The catalyst had changed color and was white and brown in places indicating that it had participated in a reaction with the olefin.

A molecular weight determination on the first fraction of the products gave a value of 44.7 indicating the presence of CO_2. The entire gaseous material was scrubbed twice through a NaOH solution to yield 4.5 g. of unreacted olefin. A check on the solution contained in the scrubber revealed the absence of fluoride ion. The apparent reaction was:

$$CF_3CF{=}CF_2 + \text{Metal oxide} = 3CO_2 + \text{Metal fluoride.}$$

On this assumption it was calculated that 30.5 g. of material should have been recovered which was in fair agreement with the 29.0 g. recovered. It was assumed that the oxygen originally mixed with the olefin did not react at all and escaped from the product trap. Four and one-half grams of olefin were recovered indicating that 29.5 g. (0.20 mole) reacted to form CO_2. Thus the recovered material should have consisted of (0.20) (44) (3) = 26.0 g. of CO_2 and 4.5 g. of olefin for a total of 30.5 g.

Since oxidative degradation took place to such a large extent a similar experiment was performed at a lower temperature.

Experiment 120 I: Forty-one and one-half grams of $CF_3CF{=}CF_2$ (0.28 mole) were mixed with 5.1 g. of oxygen (0.16 mole) in the water operated storage bottle. The 15 cm. nickel reactor was refilled with fresh Hopcalite. This material was passed through the reactor held at 200° at a flow rate of 13 cc. per min. Of a total of 46.6 g. of

reactants used, only 36.1 g. of material were recovered from the product traps. This material was transferred into the distillation column. One and six-tenths grams of a white solid were left behind as a residue in this transfer. This solid was $CF_3C(OH)_2CF_3$.

The material in the distillation column was distilled to give 16.9 g. of CO_2, 13.0 g. of unreacted olefin and 6.1 g. of material boiling above -27°. The results of the distillation can be treated as follows. The 16.0 g. of CO_2 obtained would account for (16.0/44) (1/3) = 0.12 mole of olefin oxidized. The 13.0 g. of $CF_3CF{=}CF_2$ recovered accounts for 0.09 mole of olefin. The white solid accounts for 0.01 mole of olefin using 182 as its molecular weight. This leaves 0.060 mole of material to be accounted for by the 6.1 g. of material boiling above -27°. Molecular weights on this 6.1 g. ranged from 152 to 164. Assuming an average value of 158, 0.04 mole of olefin were accounted for. This mole balance was in good agreement with the observed results. Moles of olefin used initially equaled 0.28. Moles of olefin accounted for equaled 0.26. These two experiments, 119 I and 120 I, indicated that the major process occurring over Hopcalite was:

$$CF_3CF{=}CF_2 + \text{Metal oxides} = 3CO_2 + \text{Metal fluorides.}$$

It is believed that the formation of $CF_3C(OH)_2CF_3$, rather than CF_3COCF_3, was caused by traces of moisture in

the reaction system. Possibly small amounts of CF_3COCF_3 were also formed but this compound was not detected in the free state. Since $CF_3C(OH)_2CF_3$ was formed in 3.5% yield another experiment at a lower temperature was made in an attempt to produce the anhydrous ketone as well as the hydrated form.

Experiment 122 I: Fifty-one grams of $CF_3CF{=}CF_2$ (0.34 mole) were mixed with 10.7 g. of oxygen (0.33 mole) in the water operated storage bottle. The same 15 cm. reactor repacked with fresh Hopcalite was used. The reactants were passed through the reactor held at 150° at a flow rate of 23 cc. per min. for 260 min. The temperature was increased to 180° for the remaining 480 min. of the run. Out of a total of 61.7 g. of materials used only 41 g. were recovered from the product traps. This material was transferred into the distillation column. No very low boiling material (CO_2) was isolated as in the previous run, 120 I. Thirty-nine grams of unreacted olefin, representing 77%, were recovered. Approximately 2.0 g. of a water insoluble, bluish liquid remained as a pot residue after distillation. The poor material balance observed in this run could be explained by the formation of copper or manganese salts of fluorocarbon acids which could be stable at the temperature of the run. LaZerte, et al.,[33] reported that $(C_3F_7COO)_2$ Cu decomposes at 290°-300°.

Results obtained in the oxidations over Hopcalite were unsatisfactory as were those over CuO. Useful products were not formed in appreciable quantities. The major process was found to be reaction of the Hopcalite with $CF_3CF{=}CF_2$ to give CO_2.

Experiments Performed Over NaF

Eight preliminary experiments were performed using NaF packing in the 33 cm. reactor. These experiments are tabulated in Table 2. In each run the reactants were premixed in the 27 l. water operated storage bottle to give the values reported in Column 2. Contact times listed in Column 3 are only average values as precise flow control was not maintained. In each experiment the products obtained were separated by distillation. Percentage conversion values, Column 7, were calculated from the ratio of Column 6 to Column 4. Percentage by weight of COF_2 and CF_3COF in the products, Column 8, was calculated from the total weight of products after the amount of recovered olefin was deducted. This value, for NaF, does not seem to be greatly affected by the varied operating conditions used. Since these experiments were all performed in a similar fashion only two representative runs will be discussed in detail.

Experiment 134 I: Eighty-five grams (0.57 mole) of $CF_3CF{=}CF_2$ were mixed with 16.8 g. (0.52 mole) of oxygen in the 27 l. storage container. The reaction mixture was

TABLE 2

THE REACTION OF $CF_3CF=CF_2$ WITH O_2 OVER NaF

Run No.	Reactor Temp.	Mole Ratio $O_2/CF_3CF=CF_2$	Approx. Contact Time in Seconds	Moles of $CF_3CF=CF_2$		
				Initial	Recovered	Used
	(1)	(2)	(3)	(4)	(5)	(6)
110 I	375°	0.50	248	0.35	0.09	0.26
113 I	350°	0.62	240	0.44	0.17	0.27
132 I	315°	0.85	47-136	0.53	—	0.53
134 I	280°	0.93	67	0.57	0.01	0.56
135 I	200°	1.05	168	0.23	0.23	—
136 I	250°	1.02	76	0.22	0.11	0.11
33 II	280°	1.10	52	0.22	—	0.22
64 III	301°	1.14	—	0.80	—	0.80

TABLE 2 - Continued

% Conversion to Products (7)	% by Weight of COF_2 and CF_3COF in Products (8)	% by Weight of Products Boiling Above $CF_3CF=CF_2$ (9)	Remarks
74	65	35	CF_3CF_2COF in 18.5% yield.
61	75	25	CF_3CF_2COF in 20.0% yield.
100	70	30	CF_3CF_2COF in 15.5% yield. CF_3OCF_2COF trace.
98	63	37	CF_3CF_2COF in 20% yield. CF_3OCF_2COF in 6% yield.
0	—	—	No reaction
50	63	37	No yields determined on products boiling above -26.8°. Quantity too small to fractionate.
100	76	24	CF_3CF_2COF in 9% yield. CF_3OCF_2COF in 12% yield.
100	—	—	CF_3OCF_2COF in 10% yield.

passed through the 33 cm. reactor held at 280°. The material collected in the traps amounted to 106 g. This material was distilled to give the results tabulated in Table 3.

After removal of the material boiling below -28.2°, two distinct flats were observed in the distillation curve. The product distilling from -28.2° to -26.7° was mainly CF_3CF_2COF with a trace of CF_3COCF_3 and unreacted $CF_3CF{=}CF_2$ present. The material from -10.8° to -9.6° was a previously unreported compound. This new acid fluoride was identified as CF_3OCF_2COF and gave rise to a new fluorocarbon acid containing an oxygen linkage. The unidentified pot residue was found to be water soluble and produced an acidic solution.

Product yields were estimated to be CF_3CF_2COF, 19.7%, CF_3COCF_3, 1%, and CF_3OCF_2COF, 6%. Based on the ratio of two moles of COF_2 to one mole of CF_3COF, produced by equations (6) and (7), the yields of these products were estimated to be 62.5% COF_2 and 46.4% CF_3COF.

Estimating the yields of COF_2 and CF_3COF was complicated by the fact that two moles of COF_2 were generated for each mole of CF_3COF obtained. The following reaction scheme could possibly explain this:

$$CF_3CF{=}CF_2 + O_2 = CF_3COF + COF_2 \qquad (6)$$

$$CF_3CF{=}CF_2 + 1\tfrac{1}{2}O_2 = 3COF_2. \qquad (7)$$

TABLE 3

DISTILLATION OF PRODUCTS OBTAINED IN RUN 134 I

Cut Number	Weight in Grams	Boiling Range	Possible Material	Molecular Weight
Overhead	50.5	up to -57.7°	COF_2, CF_3COF	66.8-117
1	14.2	-57.7° to -28.2°	CF_3COF, trace of $CF_3CF=CF_2$	117-152
2	18.9	-28.2° to -26.7°	CF_3CF_2COF, trace of CF_3COCF_3 and $CF_3CF=CF_2$	155-167
3	9.9	-26.7° to -10.8°	Intercut	167-180
4	5.8	-10.8° to -9.6°	CF_3OCF_2COF	180-182
Pot Residue	4.0	-9.6° and up	—	182-282

It was assumed that the excess COF_2 above that produced by equation (6) was produced by equation (7). This scheme is feasable since a material balance indicates that the additional COF_2 cannot be accounted for by oxidizing terminal CF_2 groups.

Out of 0.56 mole of $CF_3CF{=}CF_2$ consumed, 0.11 mole was converted to CF_3CF_2COF and 0.03 mole was converted to CF_3OCF_2COF. Approximately 0.06 mole was accounted for by Cut 3, Table 3, assuming this material was mainly three carbon products of average molecular weight of 174. Reaction (6) accounts for another 0.26 mole of olefin. All of these products accounted for a total of 0.46 mole of converted olefin. Only 0.11 mole of terminal CF_2 groups was left. This quantity did not account for the 0.26 additional mole of COF_2 formed, hence equation (7) is believed to be correct as this equation requires only 0.09 mole of olefin to account for the 0.26 mole of COF_2 found. Formation of COF_2 by this path would account for the remaining 0.11 mole of olefin. The agreement in mole values noted here was well within the expected error in experimental technique.

Experiment 33 II: Thirty-two and eight-tenths grams (0.22 mole) of $CF_3CF{=}CF_2$ were mixed with a 10% molar excess of oxygen gas. This mixture was passed through the 33 cm. reactor held at 280°. Upon completion of the run, 38.9 g. of material were obtained. This material was distilled to give the results listed in Table 4.

TABLE 4

DISTILLATION OF PRODUCTS OBTAINED IN RUN 33 II

Cut Number	Weight in Grams	Boiling Range	Possible Material	Molecular Weight
Overhead	20.2	-64°	COF_2, CF_3COF	67
1	9.2	-64° to -31°	CF_3COF	118-158
2	3.4	-31° to -22°	CF_3CF_2COF	158-166
3	4.8	-22° to -9.7°	CF_3OCF_2COF, Flat at -10°	166-181
Pot Residue	0.9	-9.6° and up	———	—

The 29.4 g. of COF_2 and CF_3COF were found to contain 64.4 mole percent COF_2. On the basis of reaction (6), 0.13 mole of olefin was consumed in the formation of COF_2 and CF_3COF. This left 0.09 mole of COF_2 unaccounted for. Formation of CF_3CF_2COF accounted for 0.02 mole of olefin and formation of CF_3OCF_2COF accounted for 0.03 mole. This accounted for a total of 0.18 mole of reacted olefin. Since only 0.04 mole of olefin remained unaccounted for it appeared impossible for the additional 0.09 mole of COF_2 to have been formed by the oxidation of terminal CF_2 groups. Equation (7) requires only 0.03 mole of olefin to account for the excess COF_2.

The oxidation of $CF_3CF{=}CF_2$ over NaF was felt to be gratifying since appreciable yields of useful products were formed. The major process was found to be the production of CF_3COF and COF_2. A new compound, CF_3OCF_2COF, not reported in the literature, was prepared in approximately 10% yield.

Experiments Performed Over Nickel Packing

The olefin oxidation was attempted over an inert nickel surface in order to establish whether or not the reaction observed over NaF was catalytic or thermal. It was felt that a nickel surface would not be catalytically active for the oxidation reaction. The results of these experiments are summarized in Table 5. The same procedure was observed in these runs as was used in the NaF experiments. The

TABLE 5

THE REACTION OF $CF_3CF=CF_2$ WITH O_2 OVER NICKEL

Run No.	Reactor Temp.	Mole Ratio $O_2/CF_3CF=CF_2$	Approx. Contact Time in Seconds	Moles of $CF_3CF=CF_2$		
				Initial	Recovered	Used
143 I	250°	1.02	145	0.23	0.23	—
145 I	280°	1.00	140	0.32	0.31	—
4 II	310°	1.01	143	0.29	0.16	0.13
66 II	300°	1.18	109	0.26	0.25	—
69 II	330°	1.18	95	0.25	—	0.25
70 II	300°	1.10	100	0.25	0.15	0.10

TABLE 5 - Continued

% Conversion to Products	% by Weight of COF_2 and CF_3COF in Products	% by Weight of Products Boiling Above $CF_3CF=CF_2$	Remarks
0	—	—	No detectable reaction took place.
0	—	—	No detectable reaction took place.
46	100	—	Fluoride ion test on packing neg. No high boiling products formed.
0	—	—	Fluoride ion test on packing neg. No detectable reaction took place.
97	82	18	Fluoride ion test on packing pos. High boiling products formed including 3.3% CF_3OCF_2COF.
38	—	—	Fluoride ion test on packing pos. High boiling products formed. No investigation of the high boiling material was made.

33 cm. reactor was packed with 60.5 g. of protruded 0.16 in. x 0.16 in. nickel column packing. After each run the packing was examined to ascertain whether or not NiF_2 had formed on the nickel surface.

No reaction was observed in runs 143 I and 145 I. Comparing these two experiments with runs 136 I and 33 II (Table 2) performed over NaF indicated that the NaF surface exhibited a catalytic effect. The reaction over NaF could not be due to thermal effects since the contact times over the Ni surface were approximately double those over NaF.

Thermal reaction was believed to be responsible for the oxidation that took place in run 4 II. Only two products, COF_2 and CF_3COF, were formed in this experiment. This evidence seemed to indicate that the primary reaction occurring over a Ni surface was:

$$CF_3CF{=}CF_2 + O_2 = COF_2 + CF_3COF. \qquad (8)$$

Two experiments were performed, 69 II and 70 II, so that the mole ratio of these two products could be measured in order to verify equation (8). Unfortunately, this aim was not accomplished as NiF_2 was formed on the Ni surface in both of these runs. The measured ratio was approximately one mole of CF_3COF to two moles of COF_2. The effect of NiF_2 on the reaction is illustrated by the observation that run 66 II gave no conversion whereas run 70 II gave 38% conversion. Both experiments were performed at 300°. Furthermore, no high-boiling products were observed in

run 4 II, in the absence of NiF_2, but high boiling products were formed in 69 II and 70 II where NiF_2 was known to be present.

A possible explanation of this lies in the fact that some water vapor was present in run 69 II. The products obtained in run 69 II contained a good deal of HF. The receiving trap was etched. This water vapor was introduced by changing drying tubes in the reactant stream, prior to run 69 II, and by not flushing the system out with dry nitrogen.

It was felt that the water vapor present in run 69 II hydrolyzed some of the products to form HF which at this elevated temperature attacked the Ni packing to form NiF_2 which then acted as a catalyst for the oxidation reaction in run 70 II. This observation was born out by the fact that the Ni packing gave a positive fluoride ion test and that high boiling products were obtained in runs 69 II and 70 II. No high boiling products were formed in run 4 II where fluoride ion was absent.

Experiments Performed Over CsF

Five experiments were performed over CsF. These experiments, tabulated in Table 6, offer convincing proof that inorganic fluorides catalyze the oxidation of $CF_3CF{=}CF_2$. For these runs, a 15 cm. reactor packed with 119.9 g. of CsF was used. These experiments were performed

TABLE 6

THE REACTION OF $CF_3CF=CF_2$ WITH O_2 OVER CsF

Run No.	Reactor Temp.	Mole Ratio $O_2/CF_3CF=CF_2$	Contact Time in Seconds	Moles of $CF_3CF=CF_2$		
				Initial	Recovered	Used
59 II	250°	1.10	43.5	0.17	0.17	0
61 II	280°	1.10	37.0	0.15	0	0.15
63 II	280°	1.10	34.5	0.13	0	0.13
64 II	240-250°	1.10	40.8	0.12	0.01	0.11
52 III	215°	1.14	16.0	0.79	0.33	0.46

TABLE 6 - Continued

% Conversion to Products	% by Weight of COF_2 and CF_3COF in Products	% by Weight of Products Boiling Above $CF_3CF=CF_2$	Remarks
0	—	—	No detectable reaction.
99	58	42	Reaction mixture too complex to separate by fractionation.
99	60	40	Reaction mixture too complex to separate by fractionation.
95	56	44	Reaction mixture too complex to separate by fractionation.
58	44	56	10% CF_3CF_2COF.

in the order listed. It is interesting to observe that run 59 II produced no conversion whereas run 64 II produced approximately 95% conversion despite the fact that each run was made under essentially equivalent conditions. It was noted that two runs were made at 280° where essentially complete conversion was obtained, and one run, 52 III, was made at 215° where 58% conversion was obtained. Thus it appeared that the sample of CsF used in run 59 II had no catalytic properties. From this it was concluded that catalytic properties were introduced into this sample by first initiating the oxidation reaction at a higher temperature, namely, 280°.

Experiments 61 II, 63 II and 64 II yielded mixtures of high boiling products that were not separable by distillation. This was due to the small quantities initially used and to the poor distillation characteristics of mixtures of similar fluorocarbon substances. Run 52 III was performed in an attempt to obtain a sufficient quantity of this material to permit separation by distillation. This run produced a more favorable ratio of high-boiling products to low-boiling products than did any of the other experiments. This run is discussed in some detail in the following paragraphs.

Experiment 52 III: One-hundred and eighteen grams (0.79 mole) of $CF_3CF{=}CF_2$ were reacted with 28.7 g. (0.90 mole) of oxygen over CsF at 215°. The 128 g. of products

obtained were distilled to give the results tabulated in Table 7.

The overhead material and Cut 1 were scrubbed through NaOH solution to yield 7.8 g. of unreacted olefin. The ratio of COF_2 to CF_3COF was not determined for this material. Cut 2 contained 41.4 g. of unreacted $CF_3CF=CF_2$. This $CF_3CF=CF_2$ combined with the 7.8 g. of $CF_3CF=CF_2$ recovered from Cut 1 gave 49.2 g. of unreacted olefin.

Cut 3 was assumed to be mainly CF_3CF_2COF with a trace of CF_3COCF_3 present as was the case when the oxidation was performed over NaF. This cut also contained intercut boiling up to -19.3°.

Cut 4 consisted mainly of unidentified intercut. The distillation curve for this material contained a slight inflection at -11° to -10°. This was interpreted as indicating that a small amount of CF_3OCF_2COF was present in this material.

Cut 5 was found to be essentially pure $CF_3COCF_2CF_3$. Molecular weight remained constant over the 1.4° distillation range. This ketone was made in 21% yield assuming that two molecules of $CF_3CF=CF_2$ were required for its formation.

Cut 6 contained 9.9 g. of unidentified material. This cut showed a small flat at 26.5° to 27.5° where 2.2 g. of material of molecular weight 261 were collected. The column hold up, excluding the pot residue, was pumped out of the column and also collected in this fraction. No

TABLE 7

DISTILLATION OF PRODUCTS OBTAINED IN RUN 52 III

Cut Number	Weight in Grams	Boiling Range	Possible Material	Molecular Weight
Overhead 1	41.8	-64° to -30.2°	COF_2, CF_3COF	up to 150
2	41.4	-30.2° to -28.2°	$CF_3CF{=}CF_2$	150-157
3	7.4	-28.2° to -19.3°	CF_3CF_2COF, Some CF_3COCF_3	157-170
4	10.1	-19.3° to +1.0°	Intercut, Some CF_3OCF_2COF	170-216
5	10.6	1.0° to 2.4°	$CF_3COCF_2CF_3$	216
6	9.9	2.4° to 28.5°	———	216-261
Pot Residue	5.2	up to 60°	$(CF_3)_2CFCOCF_2CF_3$	329-339

identification was made of the material boiling between 26.5° and 27.5°.

The pot residue was believed to be chiefly $(CF_3)_2CFCOCF_2CF_3$. The boiling point of this material was estimated from the pot temperature to be in the range 50° to 60°.

The results obtained by oxidizing $CF_3CF{=}CF_2$ over CsF were considered to be very significant. Considerably lower temperature was required and a greater yield of high-boiling products was obtained. This fluoride was found to be the most active of all the materials studied. Unfortunately, the complex nature of the products made it impossible to compute an acceptable material balance for the products.

The Attempted Oxidation of $CF_3CF_2CF_3$ Over CsF

The success obtained in the oxidation of $CF_3CF{=}CF_2$ over CsF led to an attempted oxidation of the saturated fluorocarbon $CF_3CF_2CF_3$. This experiment was performed in the same apparatus used for the olefin oxidations. The $CF_3CF_2CF_3$ was mixed with an equal volume of oxygen in a water operated storage bottle. This mixture was passed through a 15 cm. reactor packed with CsF. The experiment was started at 400° and the temperature was slowly raised to 620° for the last part of the experiment. Contact times varied from 45 to 35 seconds. Upon completion of the

experiment the $CF_3CF_2CF_3$ was quantitatively recovered. Thus it was concluded that this method of oxidation was unsatisfactory for saturated fluorocarbons.

Determination of the COF_2, CF_3COF Ratio

This determination was made by reaction the COF_2 and CF_3COF, obtained during the distillation of the reacting products, with a NaOH solution and then measuring the CO_2 liberated upon acidification. In each of the determinations listed in Table 8, distillate was collected until the boiling point of $CF_3CF{=}CF_2$ was reached. This distillate was combined with the material obtained overhead. These combined products were reacted with a 20%, carbonate free, NaOH solution.

The product ampule was equipped with two stopcocks so that the entire sample could be made to react by sweeping with nitrogen gas. Any unreacted material was then swept successively through Drierite and P_2O_5 drying tubes by the nitrogen stream. These products were collected in another trap, equipped with stopcocks, cooled in liquid air. This material was then degassed and weighed. In every case it was found that the unreacted material obtained in this manner was $CF_3CF{=}CF_2$. The weight of $CF_3CF{=}CF_2$ thus obtained was deducted from the original weight of products reacted to give the true weight of COF_2 and CF_3COF involved.

TABLE 8

DETERMINATION OF MOLE % COF_2, IN THE COF_2 AND CF_3COF MIXTURES, FOR SOME PRELIMINARY EXPERIMENTS

Run No.	33 II	56 II	62 II	63 II	64 II	69 II	70 II
Reaction Temp.	280°	280°	280°	280°	240°	330°	300°
Catalyst	NaF	NaF	CsF	CsF	CsF	Ni	Ni
Total Weight COF_2, CF_3COF Initial	29.4	20.4	16.3	13.7	13.0	35.3	9.8
Weight of Olefin Recovered	0.1	1.6	0.1	0.1	0.1	0.9	3.6
Total Weight COF_2, CF_3COF Corrected	29.3	18.8	16.2	13.6	12.9	34.4	6.2
Molecular Weight of CO_2	44.5	44.2	43.8	44.0	45.1	43.7	44.2
Mole % COF_2 Gravimetric	65.6	61.7	67.0	66.5	71.4	59.3	67.5
Mole % COF_2 Volumetric	64.4	61.3	65.1	66.7	62.9	59.3	64.0

The NaOH solution containing the reaction products was now slowly acidified with H_2SO_4 while stirring vigorously. The evolved CO_2 was passed successively through Drierite and P_2O_5 drying tubes. Upon completion of acidification the apparatus was flushed with nitrogen gas to insure that all the evolved CO_2 was collected in the liquid air-cooled end trap.

This CO_2 was then degassed and weighed. From this weight the amount of COF_2 originally present could be calculated. This value is listed in Table 8 in the column headed Mole Percentage COF_2 Gravimetric. This weighed quantity of CO_2 was then introduced into a calibrated volume in the vacuum system. The sample was allowed to volatilize and reach room temperature. The pressure exerted by this sample in the known volume and room temperature were then measured. Using the ideal gas relation it was then possible to calculate the amount of COF_2 originally present. Values obtained in this fashion are listed in Table 8, in the column headed Mole Percentage COF_2 Volumetric.

A molecular weight determination was made on each sample of CO_2 measured. These values are listed in Table 8, in the column labeled Molecular Weight CO_2.

As a check on this analytical procedure a blank determination was made. Twenty grams (0.13 mole) of pure $CF_3CF{=}CF_2$ were subjected to the exact procedure used in the analysis determinations. It was found that no

measurable quantity of CO_2 was evolved thus proving that the NaOH solution was carbonate free.

Examination of Table 8 shows that in each case a COF_2 to CF_3COF ratio of approximately two to one was obtained.

Some Conclusions Drawn from the Preliminary Work

The work done in this research indicated that classical oxidation catalysts such as CuO and Hopcalite are not satisfactory agents for the oxidation of fluorine containing compounds. The major process in oxidations using these materials was found to be the production of CO_2 and metal fluorides. Useful products were not isolated in appreciable yields.

Oxidations performed over inorganic fluorides were much more successful. Inorganic fluorides have an advantage over oxide type catalyst in that they do not offer a final resting site for fluoride ions. Possibly the traces of products found with the oxide catalysts used were due to the formation of fluorides which then acted as the active surface.

Experiments over NaF gave products that were totally unexpected. Most of the products found required fluorine migration to explain their structures. Considering the surfaces upon which these reactions took place this is not difficult to understand.

The oxidations over CsF were more successful than those over NaF from the standpoint of products formed. The ratio of materials boiling above $CF_3CF{=}CF_2$ to those boiling below $CF_3CF{=}CF_2$ was appreciably increased using CsF as contrasted to NaF. These two fluorides show a great difference in selectivity in the various products formed. The product CF_3OCF_2COF was formed in good yield over NaF but was not isolated over CsF. On the other hand, $CF_3COCF_2CF_3$ was not found when NaF was used but was made in good yield over CsF. The catalytic nature of this oxidation over NaF and CsF appeared to be well established. Comparison of the temperature used and the products obtained over a clean Ni surface with the results over NaF and CsF substantiated this fact.

It was felt that these preliminary experiments could be done under a controlled set of standard conditions to evaluate the relative efficiencies of the alkali fluorides as oxidation catalysts. The acidic nature of the majority of the products formed was used as the basis of analysis for the comparison experiments described in Chapter VI.

CHAPTER V

IDENTIFICATION OF PRODUCTS

Only one product of any importance, other than CO_2, was formed over the oxide catalysts. The identification of this product is discussed first. The remaining products discussed were all formed over inorganic fluoride surfaces. A number of piperazine derivatives of perhalo-acids were prepared to aid in identification of the products. The properties of these derivatives are reported in Table 12.

Identification of $CF_3C(OH)_2CF_3$

When $CF_3CF{=}CF_2$ was oxidized over CuO or Hopcalite, fine, needle like, low melting crystals were often found in the wet ice-cooled product trap. When the products contained in the Dry Ice-cooled and liquid air-cooled traps were transferred into the vacuum system more of these crystals were left behind as a residue. In experiment 65 I the crystals obtained from these two sources were combined in the vacuum system to give 0.5 g. of a solid that melted at 37° to 39° in a sealed tube under its own vapor pressure. Two determinations on the vapor showed the molecular weight to be 172 and 184 at pressures of 15.5 m.m. and 22.2 m.m.

respectively. No significance was attached to this variation in molecular weight with pressure because of the ±1.0 m.m. error in pressure readings.

This material was divided into a more volatile and a less volatile fraction in the vacuum system by sublimation. The less volatile fraction melted at 41.5° to 42.5°. This substance was water soluble and gave a neutral solution that contained no fluoride ion. A small amount of this material was used in a sodium fusion. The acidified product gave a positive fluoride ion test.

Another 0.4 g. of this solid was obtained as a residue when the volatile products from the reaction were transferred into the distillation column. This material was whiter than that obtained from the wet ice-cooled trap. This substance was water soluble, neutral, and gave a negative fluoride ion test as before. This material was divided into two fractions, by sublimation, each fraction having a melting range of 45° to 46°.

An infrared spectrum run on the first fraction showed no carbonyl band, thus eleminating the possibility of a ketone type structure. The adsorption bands observed for this substance in CCl_4 solution are noted in Table 9.

Karyakin and Nikitin[34] tabulated the infrared spectra of nine hydroperoxides and seven peroxides. They reported a hydroxyl valency vibration at 3450 cm. $^{-1}$. They found that there are no vibrations characteristic of

TABLE 9

INFRARED SPECTRUM OF $CF_3C(OH)_2CF_3$

Peak $Cm.^{-1}$	Percentage Transmission	Possible Interpretation
3550	50	-OH Valency Vibration
1210-1245	5.0	typical -C-F Adsorption
1163	15	-C-O- Stretching
925	47	≡C-O-
715	35	

≡C-O-O-C≡ although there are three frequently appearing frequencies, 860 (-O-O-), 940 and 1200 $cm.^{-1}$(≡C-O-). This solid was subjected to a modified peroxide test.[35] The negative result of this test indicated the absence of a peroxide linkage.

The problem of structure was cleared up when another sample of this unknown was prepared. From run 120 I, 1.7 g. of this material was obtained. The solid exhibited a vapor pressure of approximately 24 m.m. at 30°. The calculated molecular weight was in the range 182 to 192 allowing for an error in pressure measurement of 1.0 m.m. A melting point determination showed this material to melt in the range 44.5° to 46.0°. No change in melting range occurred when this solid was sublimed into two portions. These two portions were recombined and were repeatedly passed through a P_2O_5 drying tube. This treatment produced a low boiling liquid of molecular weight 167.

Comparison of the infrared spectrum of this gas with that of a known sample of hexafluoroacetone,[36] (theoretical molecular weight 166), showed them to be identical. Since no carbonyl band is present in the infrared spectrum of the solid and the molecular weight of the solid is different from that of the gas by about eighteen units it was felt that the formula $CF_3C(OH)_2CF_3$ was a correct representation for the structure of this product.

The formation of perfluoro-ketone hydrates has been observed before.[37-40] Generally the pure hydrates were not obtained. Hydrate formation has also been observed with the perfluoro-aldehydes. The aldehyde hydrates are reported to be isolatable as solids.[41,42] Henne[39] reported the formation of a white solid, melting below room temperature, during the distillation of CF_3COCF_3. This solid appeared wherever moist air had access to the distillation system. This solid gave a semicarbazone derivative melting very near hexafluoroacetone semicarbazone prepared from an aqueous solution. Morse[43] reported a white solid when CF_3COCF_3 was fractionated on the vacuum line. This material gave a mass spectrum identical with that of CF_3COCF_3. When sealed in a glass tube it was easily sublimed by applying the heat of the hand. They considered the substance to be a polymeric form of CF_3COCF_3 and provisionally assigned to it the structure of a trimer.

In view of the information collected in this research, it was felt that the solid observed by these

workers was merely the gem-diol form of hexafluoroacetone monohydrate.

In the course of identifying this material a polarographic reduction was performed on the second fraction of the material melting at 45° to 46°. When 0.1 N $(CH_3)_4N$ Br (aqueous) was used as the supporting electrolyte, the unknown gave a well defined reduction curve with a half wave potential of -2.02 volts with respect to a saturated calomel electrode. The nature of the reduction products was unknown.

Identification of COF_2

This product was found to be the main constituent in the material that came off overhead, past the Dry Ice-acetone cooled condenser, during distillation. In a typical experiment, 132 I, 45.9 g. of material were obtained in this fashion. A simple trap to trap, one plate distillation was made and molecular weights were determined on approximately equal fractions. The results of these determinations are listed in Table 10.

A comparison of a known[44] infrared spectrum trace of COF_2 with the infrared spectrum on the material of molecular weight 66.5 showed this substance to be COF_2 (theoretical molecular weight, 66.0). This material was found to be completely soluble in basic solution. Upon acidification, a molar quantity of CO_2 equivalent to the quantity of COF_2 dissolved was liberated.

TABLE 10

MOLECULAR WEIGHT DETERMINATIONS ON COF_2

Fraction Number	Molecular Weight	Possible Material
1	68.3	COF_2
2	66.5	COF_2
3	106.8	COF_2, CF_3COF
4	113.0	CF_3COF

Identification of CF_3COF

This material was usually found in the fraction coming off overhead from the distillation column. Relatively pure samples could be obtained through the vapor take-off outlet once the major portion of COF_2 had been removed. In a typical experiment, 33 II, a small flat was obtained at -59.5° to -59.0°. This material had a molecular weight of 117 and was believed to be pure CF_3COF (theoretical molecular weight, 116, B.P. -59°). The products coming off overhead combined with those distilling between -64° and -31° were reacted with an excess of NaOH solution. The resulting solution was neutralized with HCl. A considerable quantity of CO_2 was liberated but was not measured. After neutralization, the mixture of salts was carefully taken to dryness in a 110° oven. The dry salts were extracted with three successively smaller portions of absolute ethyl

alcohol to remove any CF_3COONa present. Evaporation of the solvent gave the sodium salt. This salt was washed into a small side arm distillation flask. Enough concentrated H_2SO_4 was added to make the concentration in the distillation flask about 50%. This solution was steam distilled and the trifluoroacetic acid liberated was collected in a small test tube containing cold propanol-2. This solution was divided into two portions. A piperazine derivative was prepared from one portion and a N-phenylpiperazine derivative was prepared from the other portion. The derivatives were recrystallized until a constant melting point was obtained. A mixed melting point determination was made for each salt with a sample of the known derivative of trifluoroacetic acid. In either case no depression of the melting point was observed.

Identification of CF_3CF_2COF

In a typical experiment 134 I, this material was contained in the cut distilling from -28.2° to -26.7°. Molecular weights on this cut ranged from 155 to 167. An infrared spectrum on the center cut of this material agreed with that reported[44] for CF_3CF_2COF (theoretical molecular weight, 166, B.P. -28).

A sample of this cut was reacted with a known quantity of water in the vacuum system. After three hours reaction time the remaining volatile material that had not

reacted was trapped in a liquid air-cooled trap. This material was dried through a P_2O_5 tube. This product was weighed and a molecular weight determination showed this material to be unreacted $CF_3CF{=}CF_2$.

The remaining hydrolyzed material was now treated with an excess of NaOH in the vacuum system. Over a period of several hours, a gas was slowly liberated. This gaseous material is discussed in the next section. The liquid remaining after NaOH treatment was neutralized with HCl and taken to dryness, care being taken to prevent overheating of the salts. The dry salts thus obtained were extracted with two portions of absolute ethyl alcohol. The ethyl alcohol was then taken to dryness and the salt obtained was again extracted with two small portions of absolute ethyl alcohol. The solvent was evaporated off to yield a quantity of sodium salt.

The free acid was liberated from this salt by acidification followed by steam distillation. A piperazine derivative was prepared from one portion of the acid and a N-phenylpiperazine derivative was prepared from another portion. These derivatives were repeatedly recrystallized to eliminate the small trace of trifluoroacetic acid derivative that was known to be a contaminant. A mixed melting point determination made for each derivative, with a sample of the known derivative, showed no depression. This information in conjunction with the boiling point,

molecular weight, and infrared spectrum was conclusive proof that this reaction product was CF_3CF_2COF.

The formation of this material in appreciable yield was considered unusual. It was felt that this material could possibly arise from the oxidation of $CF_3CF_2CF_2H$. This possibility was checked as the above mentioned hydride is often a contaminant of $CF_3CF{=}CF_2$ when prepared by the decarboxylation of $CF_3CF_2CF_2COONa$.[33]

A sample of the starting material, $CF_3CF{=}CF_2$, was dried through a P_2O_5 tube and then degassed by freezing and thawing while pumping away any evolved gases. Molecular weights taken on the first and last fraction were 149.8 and 150.1 respectively, both in good agreement with the theoretical value of 150.0. This sample was subjected to infrared analysis. The C-H bond in $CF_3CF_2CF_2H$ causes it to show adsorption[33] in the 2940 to 2990 $cm.^{-1}$ region. No adsorption band was found in this region. From the above evidence it was concluded that the starting material did not contain any appreciable quantity of hydride. Thus it was concluded that CF_3CF_2COF did not arise from the oxidation of $CF_3CF_2CF_2H$.

Identification of CF_3COCF_3

In the previous section a gas was reported liberated when the aqueous solution of products was treated with excess NaOH in the vacuum system. This gas was collected

and weighed. The molecular weight was determined to be 70.1. An infrared spectrum determination showed this material to be CF_3H (theoretical molecular weight, 70.0) which would arise from the hydrolysis[16] of CF_3COCF_3. It was impossible to separate this ketone in a pure state since its boiling point was so close to that of CF_3CF_2COF. The quantity of CF_3COCF_3 produced in this experiment, calculated from the weight of CF_3H, was about 1% of the theoretical maximum.

Identification and Proof of Structure of CF_3OCF_2COF

This new acid fluoride was contained in the fractions distilling from -10.5° to -9.5°. This material had a molecular weight of 182, fumed in air and had an unpleasant odor. This substance hydrolyzed in water with the liberation of considerable heat. A test for fluoride ion on this aqueous solution was positive.

A special piece of apparatus was constructed so that accurately weighed samples could be reacted without loss of material. Duplicate samples were reacted with a known quantity of standard NaOH solution. The aqueous solutions were back titrated with standard HCl solution to give an equivalent weight of 91. These same solutions were analyzed for fluoride ion by the thorium nitrate technique.[45] Duplicate determinations gave a value of 10.32% hydrolyzable fluoride ion. These analytical results suggested

an empirical formula of $C_3F_6O_2$ (calculated equivalent weight, 91; hydrolyzable fluoride ion, 10.44%). Chromatographic analysis indicated that this unknown was a single compound. A peroxide test performed on this material was negative and thus eliminated the possibility of a hypofluorite group. Cady[46] reported that this group reacts with KI solution to liberate iodine explosively.

An infrared spectrum on this material was determined with care being taken to maintain anhydrous conditions. The principle adsorption bands and their possible interpretations are reported in Table 11.

From the spectra trace it was apparent that a COF group was present. This point was confirmed in the neutral equivalent and fluoride ion determinations.

A sample of this unknown was treated with excess NaOH in a vacuum system. No gaseous products were evolved

TABLE 11

INFRARED ADSORPTION BANDS FOR CF_3OCF_2COF

Wave No. $Cm.^{-1}$	Percentage Transmission	Possible Interpretation
1905	1.5	C=O stretching, acid fluoride
1360-1080	0.0	typical C-F adsorption
908	3.0	
832	43.7	

indicating the absence of ketone groups. The NaOH solution was neutralized with H_2SO_4 and taken to dryness in a 110° oven. The resulting solids were extracted with absolute ethyl alcohol to yield a quantity of the sodium salt of the unknown. This sodium salt was found to be deliquescent. This salt was acidified with 50% aqueous H_2SO_4, in a small side arm flask, and the free acid was steam distilled over between 98° and 108°. The distillate was found to be free of fluoride ion. This aqueous solution had an odor resembling perfluorobutyric acid. One-half of this solution was neutralized with N-phenylpiperazine to give a water insoluble oil, as a lower layer, which after separation and drying at 110° failed to solidify. This material could not be recrystallized from the usual solvents. The other half of the solution was neutralized with anhydrous piperazine to yield an insoluble solid. This material was recrystallized from ethyl alcohol and water to give a white solid melting at 191.0° to 191.5°. These results did not agree with the properties of any of the known fluorocarbon acid piperazine salts. The results of an elemental analysis on this compound, which showed it to be $2C_3F_6O_2 \cdot C_4H_{10}N_2$, are reported in Table 12.

The two possible isomers of $C_3F_6O_2$ were CF_3CF_2OCOF and CF_3OCF_2COF. The first of these was expected to be unstable to basic hydrolysis as it would be a derivative of carbonic acid. The second isomer should be stable.

To differentiate between these two possibilities the sodium salt of a sample of the acid was prepared. This salt was decarboxylated according to the procedure of Henne[47] by refluxing for three hours in the presence of ethylene glycol. The reaction products were collected in liquid air. These products were passed through an Ascarite drying tube to remove CO_2. Molecular weights were determined on the remaining gas. The first fraction over gave a molecular weight of 134.5 and the middle fraction gave a value of 135.5. An infrared spectrum on this material indicated that it was CF_3OCF_2H (calculated molecular weight, 136). Although no information about this ether was found in the literature, its spectrum was quite similar to the spectrum of CF_3OCF_3.[48] This was considered to be proof that the structure of this unknown was CF_3OCF_2COF.

Identification of $CF_3COCF_2CF_3$

This material was contained in the fractions boiling from 0.5° to 2.0°. In a typical experiment, 52 III, distillate was collected between 1.0° to 2.4°. A molecular weight determination on the center cut of this material gave 216 (calculated molecular weight, 216). This material was water soluble, but went into solution slowly. An infrared spectrum on this material indicated the presence of a ketone carbonyl group. Holub reported[49] that $CF_3COCF_2CF_3$ boiled at 0.0°, was water soluble and gave a

semicarbazone melting at 137° to 138°, with decomposition. A semicarbazone derivative prepared on an aqueous solution of the material obtained in this work melted with decomposition at 135° to 136°. The yield of derivative was very low.

Tentative Identification of $(CF_3)_2CFCOCF_2CF_3$

This product was obtained as a pot residue. The boiling point was estimated from the pot temperature to be in the range 50° to 60°. A sample of this material was washed with water to remove traces of acidic materials. The sample was then dried through a P_2O_5 tube. Vapor density measurements showed the molecular weight to be in the range 319 to 329 (calculated molecular weight for $C_6F_{12}O$, 316). The material was washed with a dilute solution of NaOH. A gas was observed to be slowly liberated. This gas was dried through a P_2O_5 tube and collected. Upon completion of gas evolution a small amount of insoluble material remained unreacted. This unreacted material was discarded. A molecular weight determination on the evolved gas gave a value of 171. Infrared spectra determined on the first and last fractions of this material were identical. Comparison with known spectra[50] showed this material to be $(CF_3)_2CFH$ (calculated molecular weight, 170).

This hydride could have arisen from the preferential hydrolysis of $(CF_3)_2CFCOCF_2CF_3$. The symmetrical ketone $(CF_3)_2CFCOCF(CF_3)_2$ would produce only one hydride but this possibility seemed to be eliminated by its high molecular weight (366) and boiling point. Hauptschein[40] reported that $C_3F_7COC_3F_7$, an isomer of $(CF_3)_2CFCOCF(CF_3)_2$, boiled at 75°. Haszeldine[37] found that $C_3F_7COC_2F_5$, an isomer of $(CF_3)_2CFCOCF_2CF_3$, was water insoluble and boiled at 52°. This was in fair agreement with the properties of the compound found in this work. Unfortunately, the sodium salt of the other hydrolyzed portion of this molecule was discarded. The preparation of a piperazine derivative of this material would have solved the problem.

Piperazine and N-Phenylpiperazine Derivatives of Some Perhalo-Acids

In the course of this research, it was desirable to find a method for the identification of perfluoro-acids. Pollard and others[51-53] demonstrated that the salts of piperazine were very useful in the identification of organic acids.

The piperazine and N-phenylpiperazine salts of the more readily available perhalo-acids were prepared. These salts were found to be readily purified and their melting points were in a convenient range.

These derivatives and their properties are summarized in Table 12. Melting points were determined in

TABLE 12

PIPERAZINE AND N-PHENYLPIPERAZINE DERIVATIVES OF SOME PERHALO-ACIDS

Perhalo-Acid	M.P. °C Corr.	Analyses*, Percentages							
		Calculated				Found			
		C	H	F	Cl	C	H	F	Cl
Piperazinium Salts									
CF_3COOH	229-231	30.6	3.85	36.3	—	30.1	3.79	36.6	—
CF_3CF_2COOH	241-242.5	29.0	2.92	45.9	—	29.5	3.11	45.6	—
$CF_3(CF_2)_2COOH$	236-237.5	28.0	2.35	51.8	—	28.3	2.52	51.6	—
$CF_3(CF_2)_4COOH$	240.5-241.5	26.9	1.69	58.6	—	26.6	1.76	58.4	—
$CF_3(CF_2)_6COOH$	240-241	26.3	1.54	62.4	—	26.5	1.41	62.2	—
$Cl(CF_2CFCl)_2CF_2COOH$	Above 250	23.6	1.49	—	26.2	23.9	1.65	—	26.4
$Cl(CF_2CFCl)_3CF_2COOH$	Above 250	23.0	1.16	—	27.1	22.8	1.49	—	27.1
$HOOC(CF_2)_3COOH$	269-270	33.2	3.71	35.0	—	33.2	3.62	34.7	—
CF_3OCF_2COOH	191-191.5	26.9	2.76	42.6	—	27.1	2.70	42.8	—

TABLE 12 - Continued

Perhalo-Acid	M.P. °C Corr.	Analyses*, Percentages							
		Calculated				Found			
		C	H	F	Cl	C	H	F	Cl
N-Phenylpiperazinium Salts									
CF_3COOH	151-154	52.2	5.48	20.6	—	52.3	5.48	20.8	—
CF_3CF_2COOH	144-144.5	47.8	4.64	29.1	—	47.7	4.52	29.4	—
$CF_3(CF_2)_2COOH$	124-126	44.7	4.02	35.4	—	44.3	4.00	35.6	—
$CF_3(CF_2)_4COOH$	122-124	40.3	3.18	44.0	—	40.0	3.40	43.8	—
$CF_3(CF_2)_6COOH$	125.5-128	37.5	2.62	49.5	—	37.6	2.62	50.1	—
$Cl(CF_2CFCl)_2CF_2COOH$	133-134	36.6	2.88	—	20.2	36.8	3.00	—	20.1
$Cl(CF_2CFCl)_3CF_2COOH$	141-142	33.7	2.36	—	22.1	33.6	2.71	—	21.9

*Analyses by Clark Microanalytical Laboratory and Schwarzkopf Microanalytical Laboratory.

sealed tubes in a brass block which was preheated to within 5° of the melting point. The experimental procedure used in the preparation of the piperazinium salts is described in the following paragraphs.

To about 1 cc. of the acid, contained in a small beaker, was added 10 cc. of propanol-2. The beaker was placed in an ice bath, and anhydrous piperazine was slowly added with stirring until the resulting mixture was just basic to litmus paper. Another 10 cc. portion of propanol-2 was added and the slurry was filtered while cold.

The crude product was recrystallized by adding 10 cc. of 95% ethanol and adding enough water dropwise to the boiling mixture to cause the salt to dissolve. The solution was cooled in ice until crystallization was complete. This procedure was repeated four times. On the last recrystallization the solution was filtered with suction while hot. The material from the last two recrystallizations showed no change in melting point.

The piperazinium salts of $Cl(CF_2CFCl)_2CF_2COOH$, $Cl(CF_2CFCl)_3COOH$ and perfluoroglutaric acid were recrystallized from boiling water. They were extremely insoluble in all solvents, and were only successfully recrystallized in minute amounts from hot, filtered aqueous solutions.

The piperazinium salt of perfluorooctanoic acid was recrystallized by filtering a hot saturated solution of the

salt in n-butanol. This salt was extremely insoluble in all solvents.

The experimental procedure used in the preparation of the N-phenylpiperazinium salts is described in the following paragraphs.

To about 4 cc. of the acid, contained in a small beaker, was added 20 cc. of propanol-2. The beaker was placed in an ice bath. N-phenylpiperazine was slowly added to the acid solution with stirring until the resulting slurry was just basic to litmus paper. The mixture was heated until solution of the solid was complete. The crystals which separated when the flask was cooled were filtered and recrystallized four times from propanol-2. In the last recrystallization the solution was filtered while hot. The material obtained in the last two recrystallizations showed no change in melting point. The N-phenylpiperazinium salts of $Cl(CF_2CFCl)_2CF_2COOH$ and $Cl(CF_2CFCl)_3COOH$ were recrystallized from absolute ethanol.

CHAPTER VI

COMPARISON EXPERIMENTS

General Procedure Used in the Comparison Experiments

Sufficient oxygen was included in the feed mixture to insure essentially complete oxidation if the conditions of temperature and contact time warranted it. That sufficient oxygen was present was deduced from the major reactions that were found to occur in the preliminary experiments involving the alkali fluorides. These reactions were:

$$CF_3CF{=}CF_2 + O_2 = CF_3COF + COF_2 \quad (8)$$

$$CF_3CF{=}CF_2 + 1\tfrac{1}{2}O_2 = 3COF_2 \quad (9)$$

$$CF_3CF{=}CF_2 + \tfrac{1}{2}O_2 = CF_3CF_2COF \quad (10)$$

$$CF_3CF{=}CF_2 + \tfrac{1}{2}O_2 = CF_3COCF_3 \quad (11)$$

$$CF_3CF{=}CF_2 + O_2 = CF_3OCF_2COF \quad (12)$$

$$2CF_3CF{=}CF_2 + 1\tfrac{1}{2}O_2 = CF_3CF_2COCF_3 + 2COF_2 \quad (13)$$

$$2CF_3CF{=}CF_2 + \tfrac{1}{2}O_2 = (CF_3)_2CFCOCF_2CF_3 \quad (14)$$

This reation series accounted for about 95% of the products formed. The maximum stoichiometric ratio of oxygen to olefin occurred in reaction (9). Since this reaction only accounted for 13% to 16% of the total products it was

not necessary to use enough oxygen to satisfy this equation to insure complete oxidation. The feed material ratio of oxygen to olefin was set at 1.135. This arbitrary ratio was used for all of the comparison experiments. This mixture was prepared by adding a given quantity of olefin to the calibrated 27 l. storage bottle. The calculated amount of oxygen was then added, from a storage cylinder, in the same manner. A small quantity of water was always left in the storage bottle so that the gases could be intimately mixed by vigorous agitation of this water. This standard mixture was then metered into the reactor at the desired flow rate.

Prior to starting a series of experiments, the reactor and catalyst were evacuated at 400° for two hours by pumping through a liquid air trap. Upon completion of this treatment dry nitrogen was admitted to bring the pressure in the reactor up to atmospheric.

Reaction products were collected in a liquid air cooled glass trap, equipped with stopcocks. Upon completion of a run the reaction system was flushed with dry nitrogen for 15 min. to insure that all products were collected in the end trap. This trap was now connected to the vacuum line and any unreacted oxygen was removed by a process of pumping, thawing, refreezing and then repumping until all noncondensables were removed. The total weight of products was then recorded.

This trap was connected to the analytical system where the products were passed through a 20% NaOH solution. Upon completion of this scrubbing the reaction train was swept with nitrogen for 20 min. This procedure swept all unreacted substances successively through Drierite and P_2O_5 drying tubes into the end trap which was immersed in liquid air. This trap was degassed and the contents weighed. The material recovered in this fashion was assumed to be only $CF_3CF{=}CF_2$. From this value and the calculated amount of olefin used initially it was possible to compute a percentage conversion value.

In each series of runs involving the alkali fluorides the oxidation reaction was initiated at a temperature considerably higher than that required for reaction once the catalyst had been activated. It was found that the best reproducibility was obtained when the runs over the alkali fluoride salts were performed in order of decreasing temperature.

The weighing technique used in these runs introduced some error into the percentage conversion values. A new triple beam balance, reading to 0.1 g., was used in all weighings. The traps containing products were cooled in liquid air to about one inch above the product level. The remainder of the trap was dried with a soft cloth and any ice adhering to the cold portion was removed before weighing. This same technique was used to obtain empty weights on the

traps. All weights were recorded to the closest 0.1 g.

As pointed out in Chapter II, an individual reactor was built for each salt. The dimensions of these reactors were held constant in order to minimize geometry effects. Contact times were held as constant as was feasable in an attempt to eliminate as many process variables as was possible.

It was found that special care had to be taken in loading the reactors containing KF, RbF and CsF because of the extremely deliquescent nature of these materials. CsF was especially bad in this respect. A special copper funnel was made to fit snugly inside the inlet tube of the reactor and yet not reduce the size of the opening appreciably. Prior to loading one of the salts into the reactor it was dried on a hot plate at 350° in a platinum vessel. A heat lamp was placed directly over this vessel to help keep the salt dry. The hot, dry salt was then transferred by spatula into the copper funnel, attached to the dry reactor, which was heated by the heat lamp. If this procedure was not observed it was found that these deliquescent salts would sinter into one hard lump in the reactor upon heating even though they appeared dry when loaded into the tube.

The deliquescent nature of these salts made it difficult to maintain a constant flow rate because end plugs would form where the reactant gases were admitted to the reactor. These plugs increased the pressure drop across

the reactor and therefore interefered with the Flowrator calibration. These difficulties were minimized after some experience had been obtained in running the equipment. Information pertaining to the individual catalysts and reactors used in the comparison experiments is found in Table 13.

In Figures 2-9 each run number has a point number associated with it. Point numbers are used to clarify the text associated with each figure. Point numbers indicate the sequence in which the experiments were performed.

Comparison Experiments Using LiF

Twelve experiments were performed over a new sample of LiF. These experiments are tabulated in Table 14. Considerable difficulty was encountered with this salt in maintaining activity. Fig. 2 indicates that experiments 92 II and 93 II (represented by points 1 and 2) were performed before the catalyst was activated. Maximum activity was assumed to have been obtained after completion of experiment 94 II. These experiments were performed on the same day. Points 4, 5, 6 and 7 were determined on the following day and show no irregularities. The catalyst was then allowed to stand at 200° in an atmosphere of dry nitrogen for three days. Points 8 and 9 were then determined. These two experiments clearly show that the catalyst had lost activity. The catalyst was then reactivated at

TABLE 13

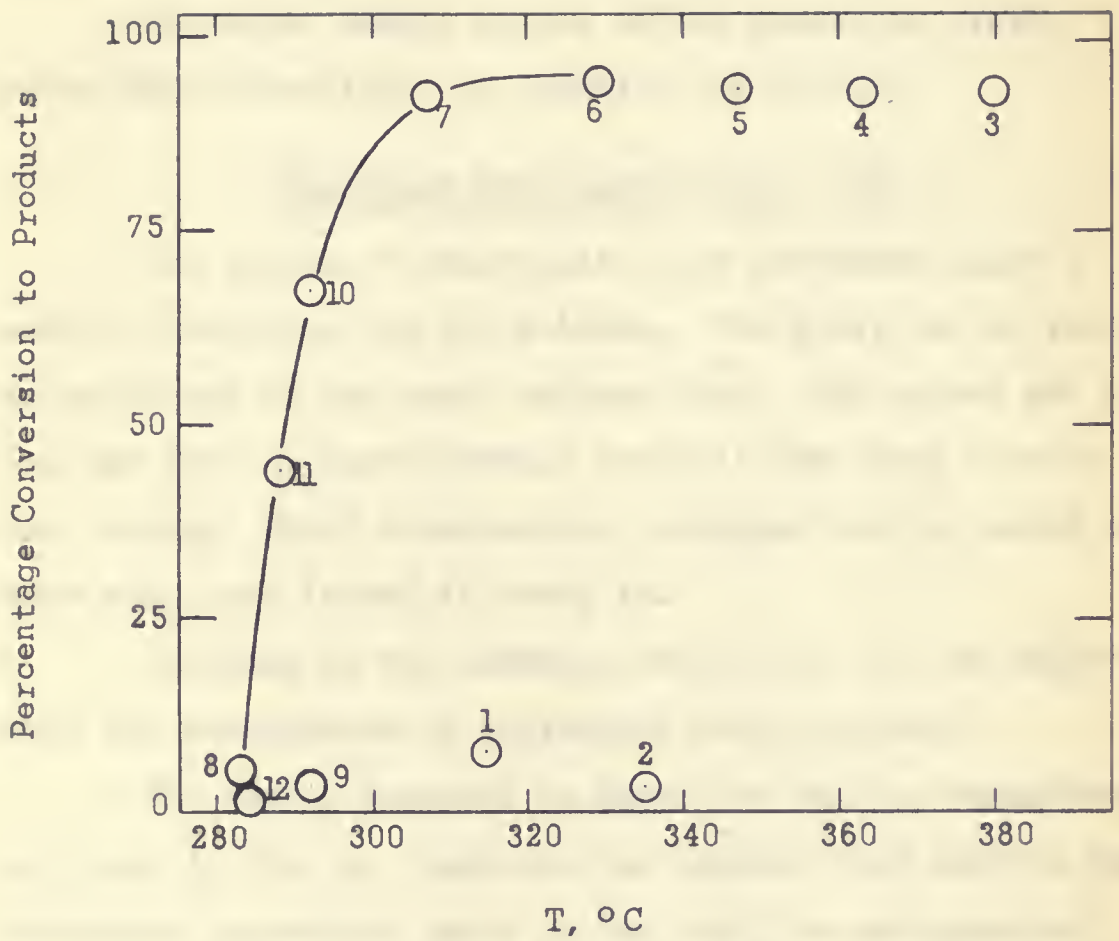
REACTOR AND CATALYSTS DATA, COMPARISON EXPERIMENTS

Catalyst	Catalyst Form	Catalyst Density g./cc.	Total Wt. Catalyst g.	Catalyst Vol. cc.	Reactor Vol. Empty cc.	Reactor Vol. Packed cc.
LiF	Powder	2.32	35.8	15.4	52.1	36.7
NaF	Pellets	2.50	55.3	22.1	52.1	30.0
KF	Granular	2.30	72.6	31.6	52.1	20.5
RbF	Granular	3.35	73.5	21.9	52.1	30.2
CsF	Granular	3.95	119.9	30.3	52.1	21.8
Ni	Protruded Packing	8.9	42.6	4.8	53.9	49.1
CaF_2	Powder	3.2	59.2	18.6	52.1	33.5
BaF_2	Powder	4.8	68.0	14.1	52.1	38.0

TABLE 14

DATA FROM COMPARISON EXPERIMENTS OVER LiF

Run No.	Temp.	Contact Time Sec.	Dry Vol. Feed Mixture Used cc.	Calc. Wt. of Olefin Used g.	Total Wt. Products Formed g.	Wt. of Olefin Recovered g.	% Conv. to Products
92 II	324.5°	24.8	2875	8.1	8.0	7.4	9
93 II	345°	25.0	2875	8.1	8.0	7.8	4
94 II	380°	25.3	3833	10.8	12.9	0.6	94
95 II	363°	22.0	3823	10.8	13.4	0.6	94
96 II	347°	25.7	3823	10.8	13.4	0.7	94
97 II	329°	26.5	3823	10.8	13.1	0.5	95
98 II	307.5°	24.4	3823	10.8	13.1	0.8	93
99 II	282.5°	25.8	1911	5.4	5.2	5.1	6
100 II	292°	32.1	1911	5.4	5.5	5.2	4
101 II	292°	27.9	2875	8.1	9.4	2.6	68
102 II	288°	26.6	1911	5.4	5.9	3.0	44
104 II	284°	24.5	1911	5.4	5.6	5.3	2



Run No.	Point No.	Run No.	Point No.
92 II	1	98 II	7
93 II	2	99 II	8
94 II	3	100 II	9
95 II	4	101 II	10
96 II	5	102 II	11
97 II	6	104 II	12

Fig. 2. Comparison Experiments Using LiF

350° by passing two liters of the reaction mixture through the reactor. After reactivation, points 10, 11 and 12 were determined.

Molecular weight checks on the unreacted olefin showed that essentially no impurity was present.

Comparison Experiments Using NaF

Two series of experiments were performed using a reactor containing new NaF pellets. The first set of runs was performed at the usual contact time. The second set of runs was done at approximately one-half the usual contact time values. These experiments, performed over a period of three days, are listed in Table 15.

Contrary to the behavior noted with LiF, no difficulty was encountered in activating this fluoride.

The curves obtained in these two sets of experiments are shown in Fig. 3. Reducing the contact time shifted the percentage conversion curve to the right as was expected. The small shift observed in these two sets of runs indicated that minor variations in contact time, within a given set of runs, did not greatly affect the shape of the curve.

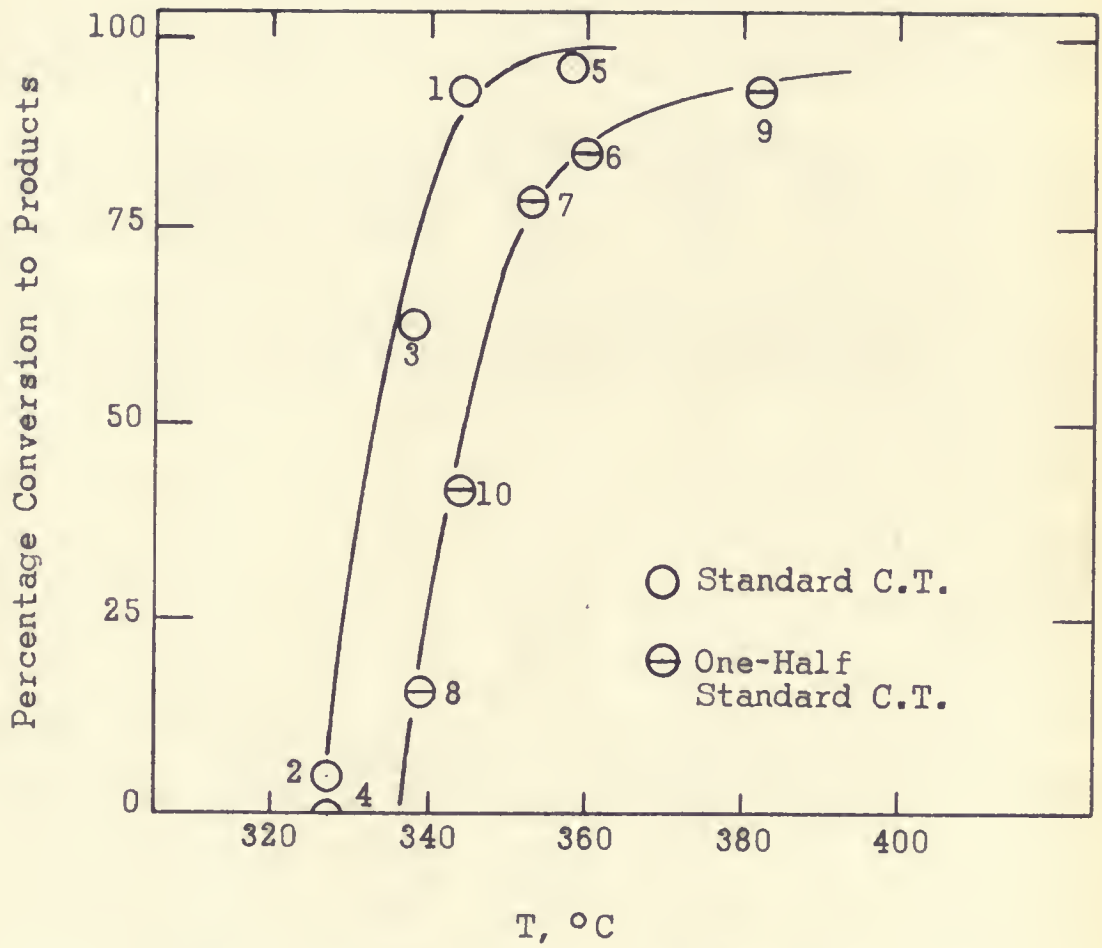
Comparison Experiments Using KF

The six experiments performed over KF are tabulated in Table 16. The last four runs which determined the conversion curve, shown in Fig. 4, were done in one day. No

TABLE 15

DATA FROM COMPARISON EXPERIMENTS OVER NaF

Run No.	Temp.	Contact Time Sec.	Dry Vol. Feed Mixture Used cc.	Calc. Wt. of Olefin Used g.	Total Wt. Products Formed g.	Wt. of Olefin Recovered g.	% Conv. to Products
Experiments at Standard Contact Time							
106 II	344°	22.7	1911	5.4	6.5	0.4	93
108 II	327°	18.8	2867	8.1	8.3	7.7	5
109 II	337.5°	19.9	1911	5.4	5.6	2.0	63
110 II	326.5°	20.8	2007	5.8	5.8	5.9	0
111 II	358°	18.7	3823	10.8	13.4	0.4	96
Experiments at One-half Standard Contact Time							
112 II	360°	9.3	2875	8.1	10.2	1.2	85
113 II	353°	9.5	2875	8.1	10.0	1.7	79
114 II	339°	9.3	2395	6.8	7.3	5.7	16
115 II	382°	10.4	3248	9.2	11.2	0.6	93
116 II	344°	9.8	2875	8.1	8.8	4.7	42



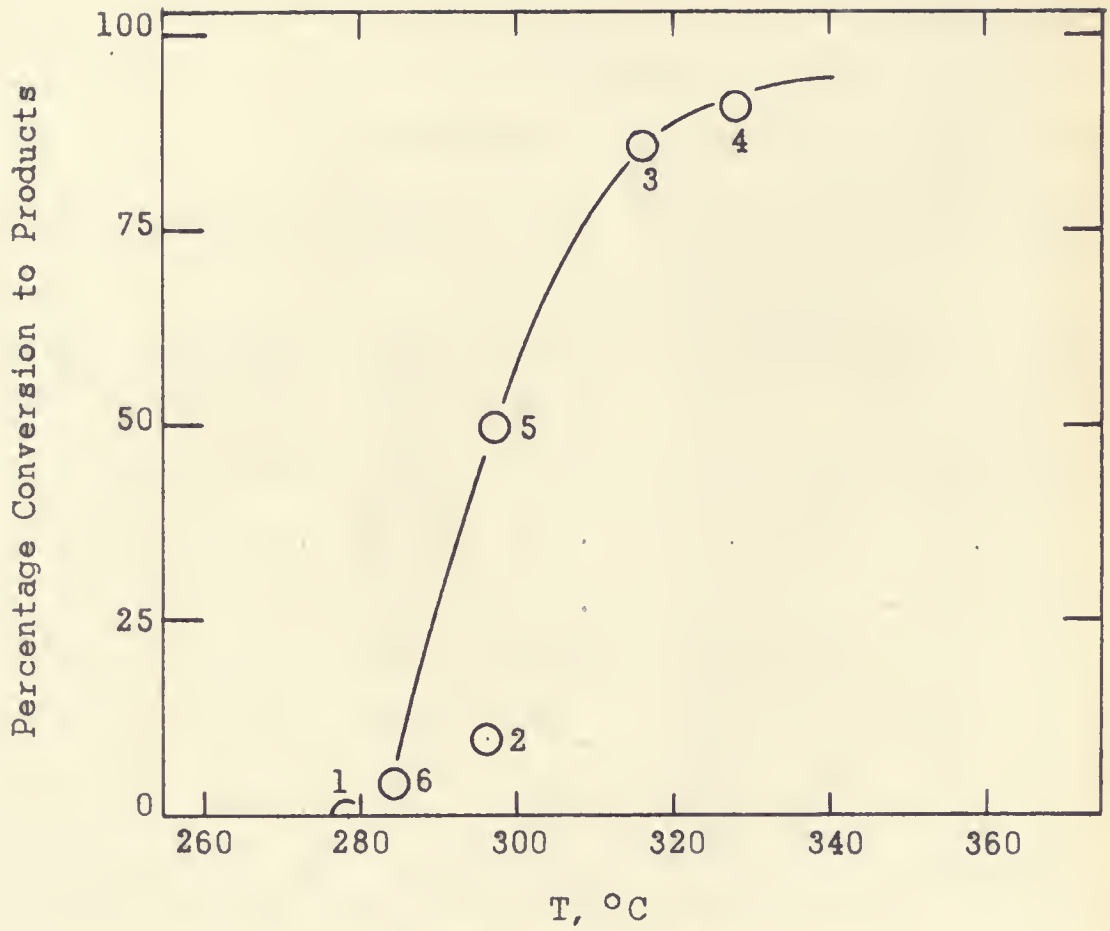
Run No.	Point No.	Run No.	Point No.
106 II	1	112 II	6
108 II	2	113 II	7
109 II	3	114 II	8
110 II	4	115 II	9
111 II	5	116 II	10

Fig. 3. Two Sets of Comparison Experiments Using NaF

TABLE 16

DATA FROM COMPARISON EXPERIMENTS OVER KF

Run No.	Temp.	Contact Time Sec.	Dry Vol. Feed Mixture Used cc.	Calc. Wt. of Olefin Used g.	Total Wt. Products Formed g.	Wt. of Olefin Recovered g.	% Conv. to Products
85 II	278°	20.4	3823	10.8	10.9	10.8	0
86 II	296°	19.9	2867	8.1	—	7.3	10
87 II	316°	19.7	3823	10.8	12.8	1.5	86
88 II	328°	19.2	1911	5.4	6.6	0.5	91
89 II	297°	20.1	1911	5.4	6.0	2.7	50
90 II	284°	20.3	2867	8.1	8.3	7.8	4



Run No.	Point No.
85 II	1
86 II	2
87 II	3
88 II	4
89 II	5
90 II	6

Fig. 4. Comparison Experiments Using KF

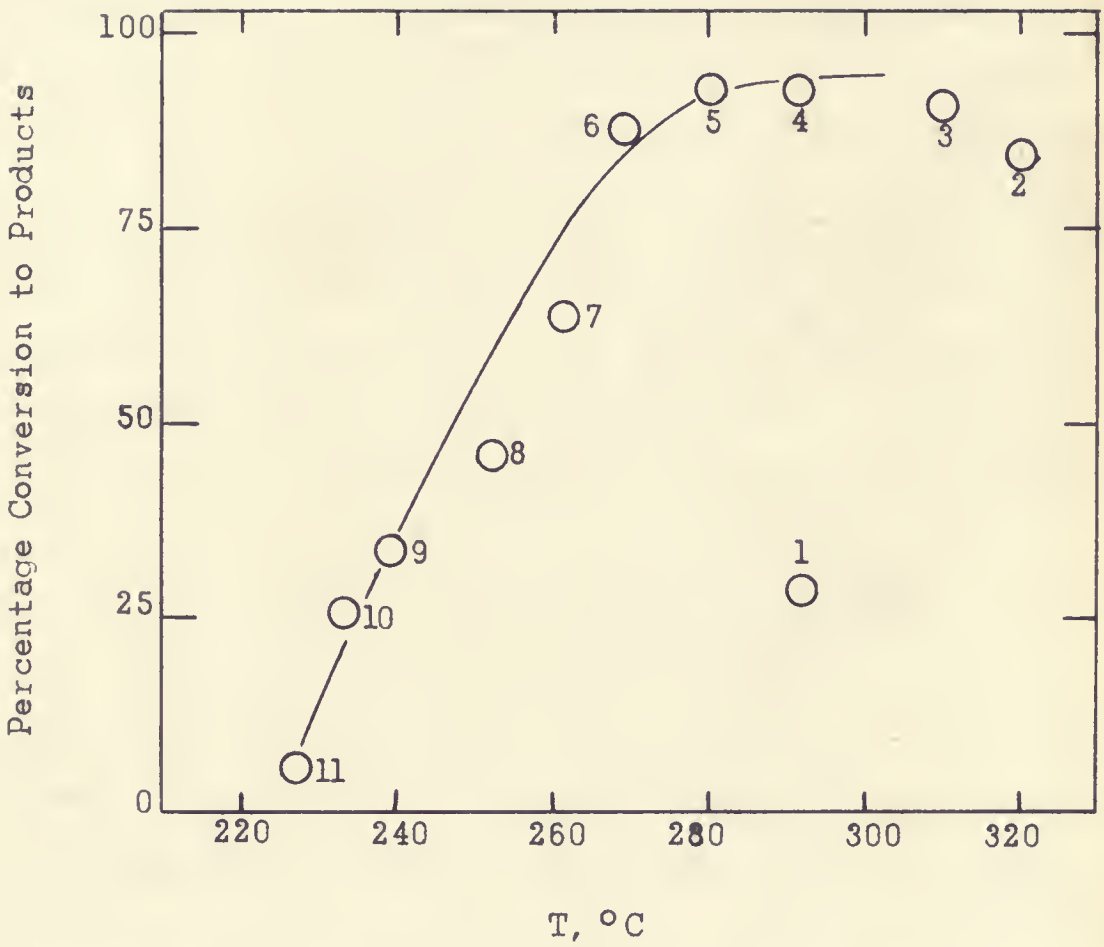
previous experiments had been done with this KF containing reactor. The first experiment, run 85 II, produced no conversion. The temperature was raised to 380° and reaction was initiated. Two liters of mixture were allowed to pass through the reactor at this temperature. The reactor was then swept out with nitrogen and run 86 II was performed. Maximum activity had not yet been attained. The catalyst was successfully reactivated by again raising the temperature to 380° and allowing four liters of reactant mixture to flow through the reactor. Four more points were then determined.

Molecular weight checks on the recovered olefin showed essentially no impurity to be present.

Comparison Experiments Using RbF

This reactor contained new, unused RbF. The activation behavior of RbF was similar to that of LiF. RbF was not active until reaction was initiated and maintained at a higher temperature than was required for reaction over the activated catalyst.

Activation required initiation of the reaction at 380°. Approximately four liters of the feed mixture were passed through the reactor before activity was obtained. Fig. 5 shows the result of insufficient activation of the catalyst on the activity. From this figure it can be seen that points 1, 2 and 3 were determined before the catalyst was at maximum activity.



Run No.	Point No.	Run No.	Point No.
120 II	1	126 II	7
121 II	2	127 II	8
122 II	3	128 II	9
123 II	4	129 II	10
124 II	5	131 II	11
125 II	6		

Fig. 5. Comparison Experiments Using RbF

TABLE 17

DATA FROM COMPARISON EXPERIMENTS OVER RbF

Run No.	Temp.	Contact Time Sec.	Dry Vol. Feed Mixture Used cc.	Calc. Wt. of Olefin Used g.	Total Wt. Products Formed g.	Wt. of Olefin Recovered g.	% Conv. to Products
120 II	292°	24.2	2895	8.2	—	5.8	29
121 II	319.5°	24.5	3860	11.0	12.6	1.6	85
122 II	310°	24.4	3860	11.0	13.4	1.0	91
123 II	291°	22.8	3860	11.0	12.8	0.8	93
124 II	280°	25.2	3860	11.0	12.9	0.8	93
125 II	269°	24.6	3860	11.0	13.3	1.3	88
126 II	260.5°	24.8	3842	10.9	12.4	3.9	64
127 II	252°	23.2	3842	10.9	11.8	5.9	46
128 II	238.5°	24.2	3842	10.9	11.6	7.2	34
129 II	233°	25.0	2407	6.8	7.4	5.0	26
131 II	227°	23.9	3842	10.9	11.0	10.2	6

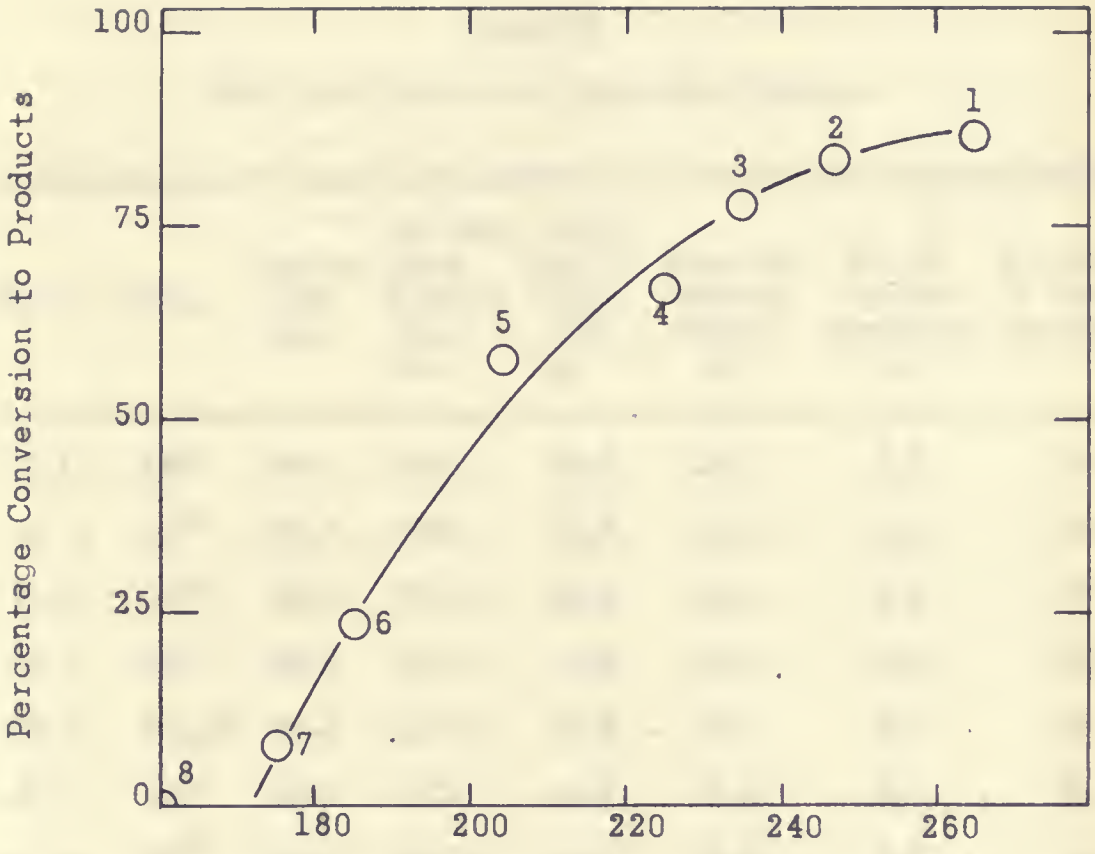
Eleven experiments, reported in Table 17, were done with RbF in order of decreasing temperature. These runs were performed over a period of five days. No loss in activity was observed due to the catalyst sitting idle. During periods when no experiments were being performed, the catalyst was maintained at 200° in an atmosphere of nitrogen.

Some relatively non-volatile products were formed over RbF in the temperature range 240° to 270°. Molecular weight checks on the recovered starting material indicated that some impurities were present.

Comparison Experiments Using CsF

The reactor containing CsF had previously been used in four preliminary experiments. These experiments were runs 59 II, 61 II, 63 II and 64 II. The results of these experiments showed that this catalyst was activated. Nine runs were made over a period of five days with CsF. Fig. 6 shows that no loss of activity occurred with this catalyst during this time. When no reaction was being performed, the catalyst was maintained at 200° in an atmosphere of nitrogen. The conditions used and the results obtained in these experiments are listed in Table 18.

When the material in the product traps from runs 77 II, 78 II and 79 II was being analyzed it was noted that some of the products were not swept through the analysis system even by nitrogen. No attempt was made to force this



Run No.	Point No.
75 II	1
76 II	2
77 II	3
79 II	4
80 II	5
81 II	6
82 II	7
83 II	8

Fig. 6. Comparison Experiments Using CsF

TABLE 18

DATA FROM COMPARISON EXPERIMENTS OVER CsF

Run No.	Temp.	Contact Time Sec.	Dry Vol. Feed Mixture Used cc.	Calc. Wt. of Olefin Used g.	Total Wt. Products Formed g.	Wt. of Olefin Recovered g.	% Conv. to Products
75 II	265°	28.0	3832	10.8	11.8	1.4	87
76 II	247°	30.0	3823	10.8	12.6	1.7	84
77 II	235°	28.9	3823	10.8	12.5	2.4	78
79 II	225°	24.8	3823	10.8	12.0	3.6	67
80 II	203.5°	25.6	3823	10.8	11.9	4.6	58
81 II	185°	26.5	3812	10.7	11.0	8.1	24
82 II	175°	27.4	3812	10.7	11.0	9.8	8
83 II	160°	28.6	3823	10.8	11.1	11.1	0

non-volatile substance through the NaOH solution as this material was obviously not olefin. These non-volatile products were probably the same as those found in the preliminary experiments and would contribute some error to the percentage conversion values. Although no measurement of quantities involved was made, there appeared to be more non-volatile material formed over CsF than RbF. Assuming ketones to be present, as was the case in the preliminary experiments, their hydrolysis in the analysis system would give rise to unreactive hydrides. These hydrides along with all other unreactive products that entered the analysis system were swept into the end trap and were weighed as unconverted $CF_3CF{=}CF_2$. Molecular weight checks showed that some material other than $CF_3CF{=}CF_2$ was present in the material recovered from the runs over CsF.

Comparison Experiments Using Nickel

The nickel reactors used in the preceding experiments appeared to be exceedingly resistant to attack from the reaction products at temperatures up to 380°. In view of this a nickel surface was tried in the belief that it would not be active for the oxidation reaction. It was felt that this experiment would establish an upper temperature limit where thermal reaction would set in.

Four runs were made with a reactor that initially contained clean nickel packing. These runs are tabulated

in Table 19. From Fig. 7 it is seen that nickel packing became active after two runs were made. This activity was caused by the nickel surface becoming coated with NiF_2. A fluoride ion test performed after experiment 36 II was positive although there was very little change in the physical appearance of the nickel packing.

Comparison Experiments Using CaF_2

Four runs were performed with the reactor containing CaF_2. These runs are tabulated in Table 19, and the conversion curve is shown in Fig. 8. Run 50 II seemed to indicate that this surface also became active after use. However, no further experiments were performed to verify this.

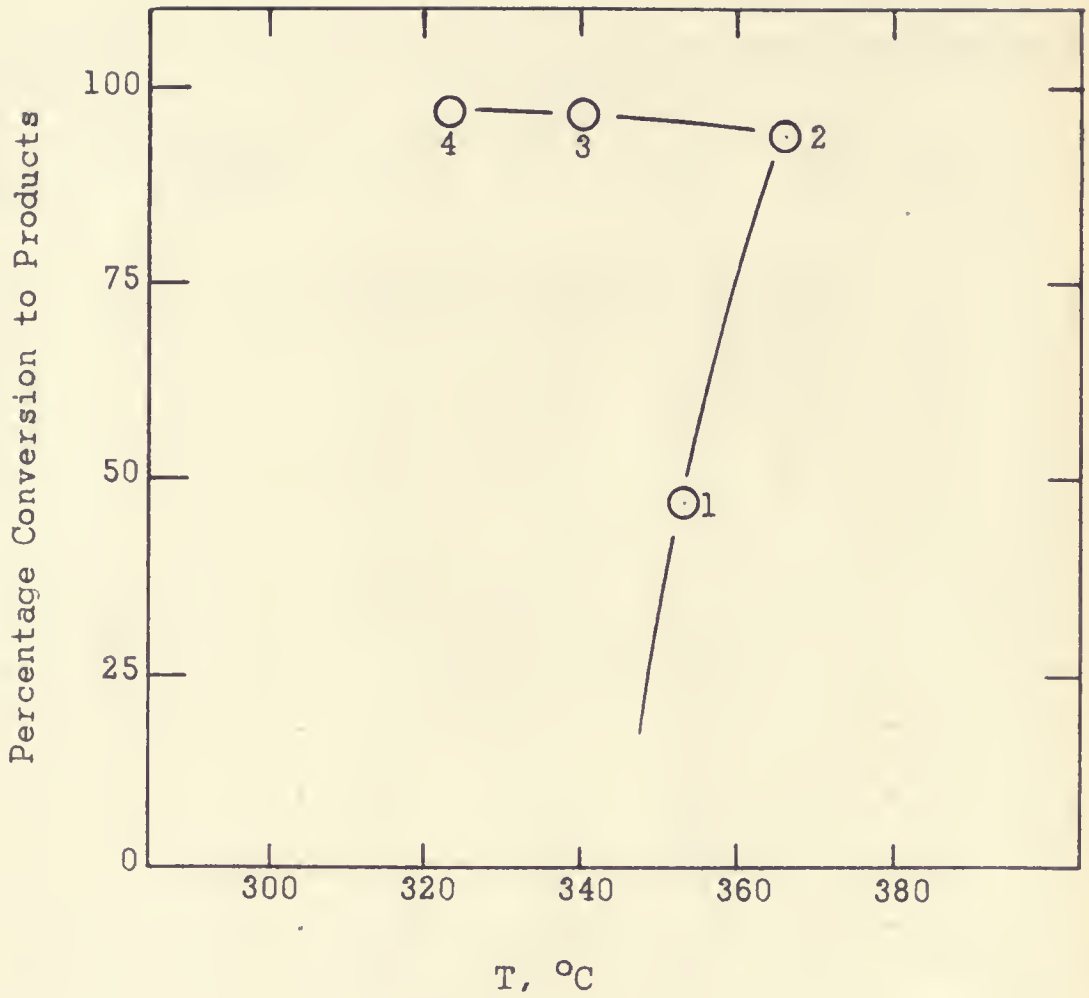
Comparison Experiments Using BaF_2

Seven runs were performed over BaF_2. These runs are tabulated in Table 19. These experiments fell into two groups. Fig. 9 shows that experiments 39 III, 40 III and 41 III determine one curve and experiments 42 III, 43 III and 44 III determine another similar curve. The first group of runs (39 III, 40 III and 41 III) were performed on the same day. The second group (42 III, 43 III and 44 III) were performed one day later. These two curves merge at high percentage conversion values. It is possible that the variation between these two sets of data is within the

TABLE 19

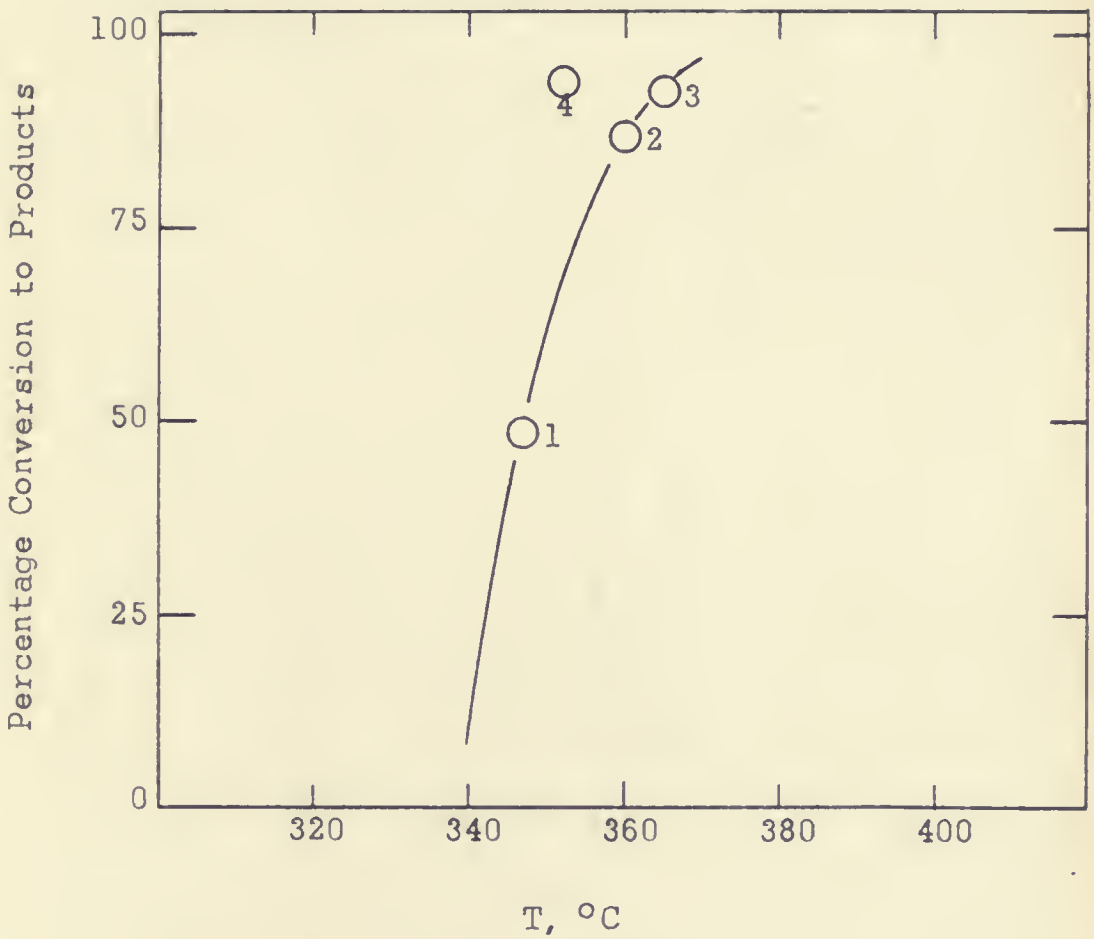
DATA FROM COMPARISON EXPERIMENTS OVER Ni, CaF_2 AND BaF_2

Run No.	Temp.	Contact Time Sec.	Dry Vol. Feed Mixture Used cc.	Calc Wt. of Olefin Used g.	Total Wt. Products Formed g.	Wt. of Olefin Recovered g.	% Conv. to Products
			Experiments Using Ni Packing				
33 III	352.5°	23.5	3851	10.9	11.6	5.8	47
34 III	365.5°	22.0	3851	10.9	13.1	0.7	94
35 III	340°	22.2	3851	10.9	12.6	0.3	97
36 III	323°	22.8	3851	10.9	13.2	0.3	97
			Experiments Over CaF_2				
47 III	347°	22.1	2881	8.2	8.2	7.8	49
48 III	360°	22.1	2881	8.2	9.4	1.1	87
49 III	365°	23.9	2881	8.2	10.0	0.6	93
50 III	352°	22.6	2881	8.2	9.3	0.5	94
			Experiments Over BaF_2				
38 III	329°	25.0	2881	8.2	8.1	8.1	0
39 III	347°	22.7	2881	8.2	8.3	6.4	18
40 III	358°	20.3	2888	8.2	9.8	1.6	80
41 III	370°	20.3	2888	8.2	9.6	0.9	89
42 III	353°	22.1	2881	8.2	8.4	7.5	8
43 III	361°	22.6	2881	8.2	9.8	3.1	62
44 III	367°	20.9	2881	8.2	9.7	1.2	85



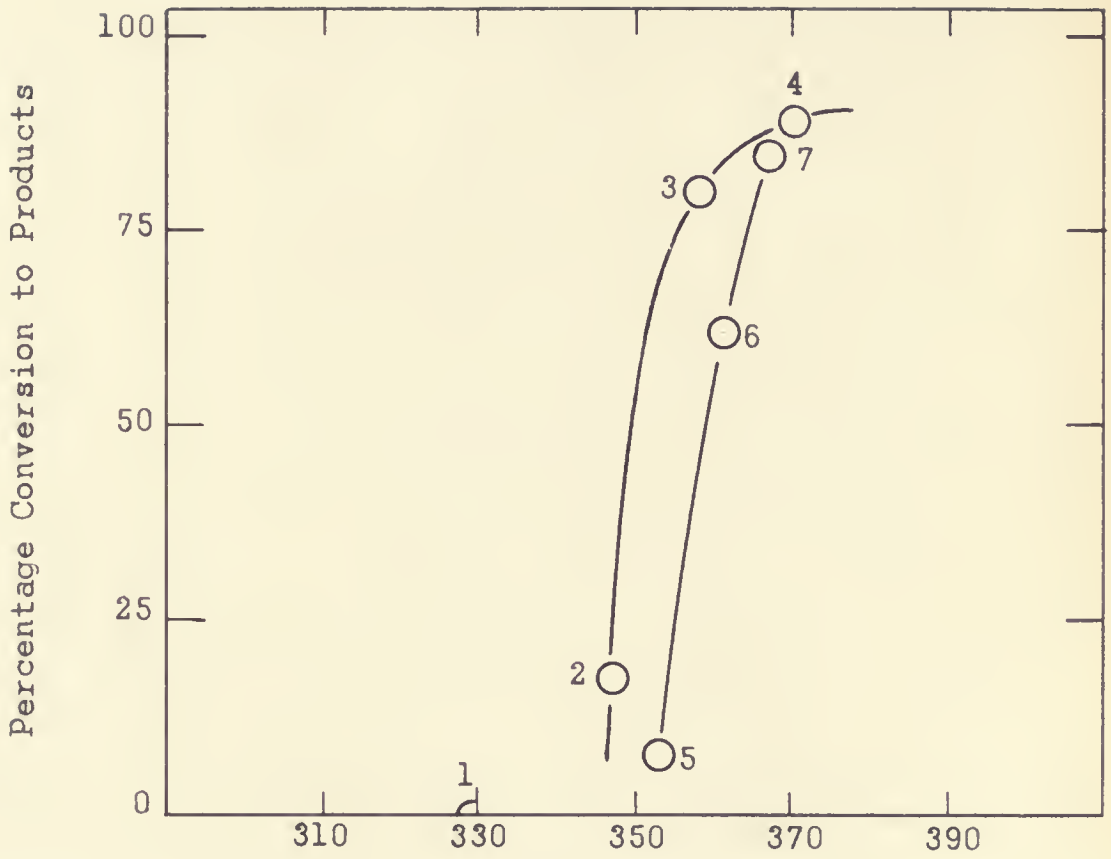
Run No.	Point No.
33 III	1
34 III	2
35 III	3
36 III	4

Fig. 7. Comparison Experiments Using Ni



Run No.	Point No.
47 III	1
48 III	2
49 III	3
50 III	4

Fig. 8. Comparison Experiments Using CaF_2



Run No.	Point No.
38 III	1
39 III	2
40 III	3
41 III	4
42 III	5
43 III	6
44 III	7

Fig. 9. Comparison Experiments Using BaF_2

experimental error inherent in the methods used in their determination. The second curve in Fig. 9 lies to the right of the first curve showing that this fluoride was not activated with use.

CHAPTER VII

DISCUSSION OF RESULTS

The work done in the preliminary experiments indicated that CuO and Hopcalite were unsatisfactory as oxidation catalysts for fluorine-containing compounds. The major process occurring over these surfaces was oxidative degradation of the starting material with simultaneous production of CO_2.

Fluorine exchange studies with $CF_3CF{=}CF_2$ and various alkali fluorides suggested that these salts might function as catalysts. This premise was based on the fact that the exchange reaction involved rearrangement of the chemical bonds in $CF_3CF{=}CF_2$. The intermediate rearrangement species should react with oxygen to form products.

Results of the preliminary experiments showed that the alkali fluorides were good catalysts for the oxidation reaction. NaF and CsF were studied extensively since these two fluorides showed a significant difference in rate of fluorine exchange with $CF_3CF{=}CF_2$.

The results obtained in the comparison experiments are best illustrated in the summary plot, Fig. 10. The

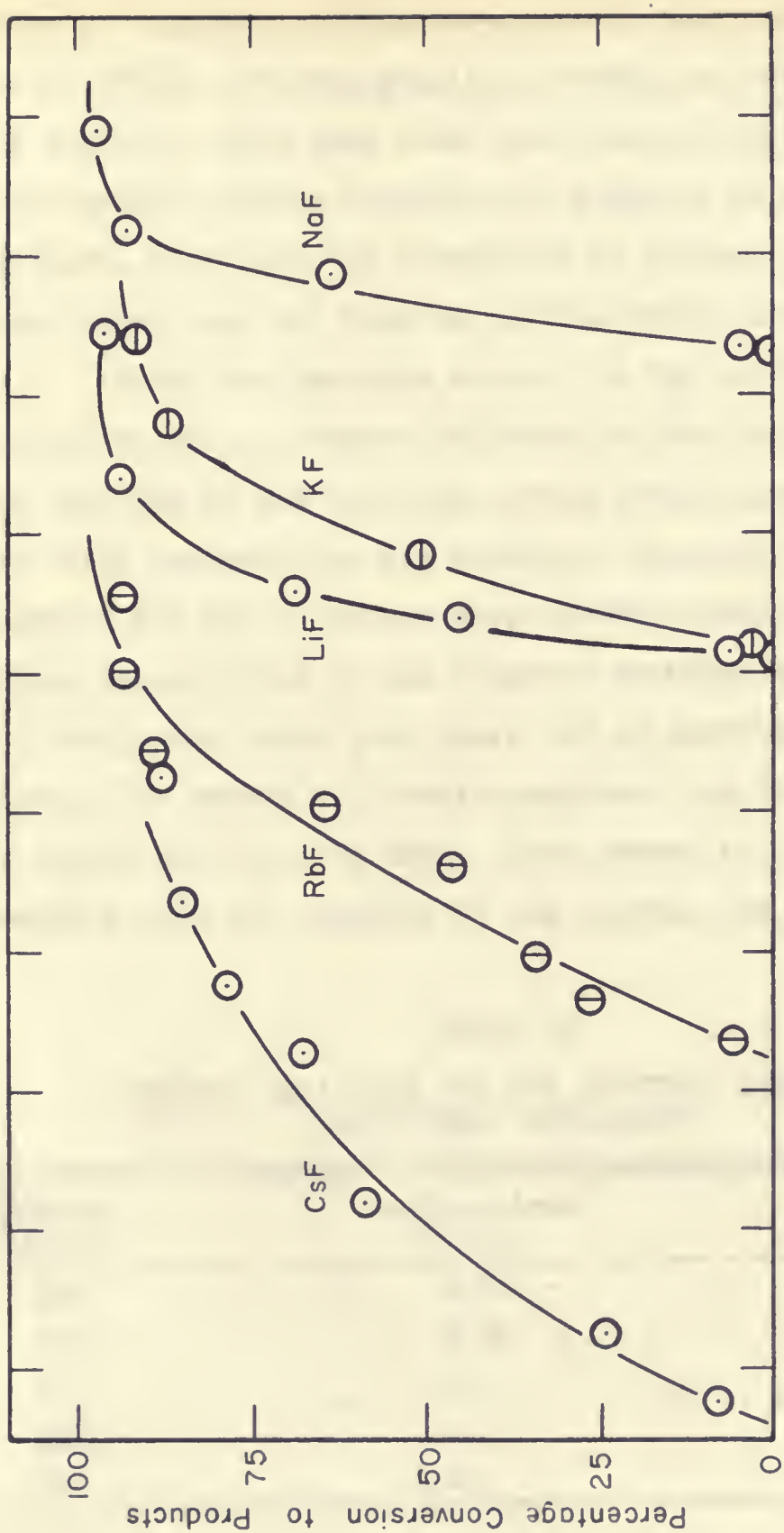


Fig. 10. Summary Plot; Percentage Conversion as a Function of T°C for the Alkali Fluorides

order of fluorine exchange observed by Gens and Wethington[22] for $CF_3CF{=}CF_2$ with the alkali fluorides was CsF>RbF>KF, NaF and LiF. This same order was observed in the oxidation experiments. Cesium fluoride was found to be a better catalyst, both from the standpoint of products obtained and temperature required than any of the other materials studied.

Total surface area present in the reactor (Table 20) did not exert any obvious influence on the reaction as CsF, RbF and KF had both the lowest surface area per gram and total surface area per reactor. Apparently this reaction was not a surface area limited process. This same effect was observed in the fluorine exchange work. Gens and Wethington found that there was no definite relation between the amount of fluorine exchange and the surface area of the alkali fluoride used. This seemed to indicate that reaction with the interior of the crystal was involved since

TABLE 20

SURFACE AREA DATA FOR THE REACTORS USED IN THE COMPARISON EXPERIMENTS

Reactor Packing	Surface Area M.2/g.	Total Area M.2/Reactor
LiF	0.69	25.2
NaF	0.38	21.0
KF	<0.1	<7.3
RbF	<0.1	<7.4
CsF	<0.1	<12.0

exchange values larger than expected from the surface area were obtained in the fast exchange reaction reported by these workers.

A plot of log percentage conversion versus reciprocal absolute temperature revealed several significant facts concerning the alkali fluorides. For each conversion curve, Fig. 11 showed two linear regions. The low conversion values and the very high conversion values were linear. The intermediate values seemed to curve slowly from one linear region to the other. The intersection of the two linear regions was determined by extrapolation. These intersections established a temperature for each alkali fluoride that was found to be very nearly the expected Tammann temperature[54] for these salts. Rees[55] described the Tammann temperature as the temperature of onset of mobility of lattice ions or atoms. This temperature, approximately one-half the absolute melting point, does not represent a discontinuity of behavior, but represents an area in which rapid migration of ions and atoms becomes possible.

The experimentally determined intersection values from Fig. 11 are tabulated in Table 21 and are compared to similar values obtained from Fig. 10 by determining the temperature at which zero conversion took place. The ratio of the intersection value to the absolute melting point was calculated for each alkali fluoride. In each case this value

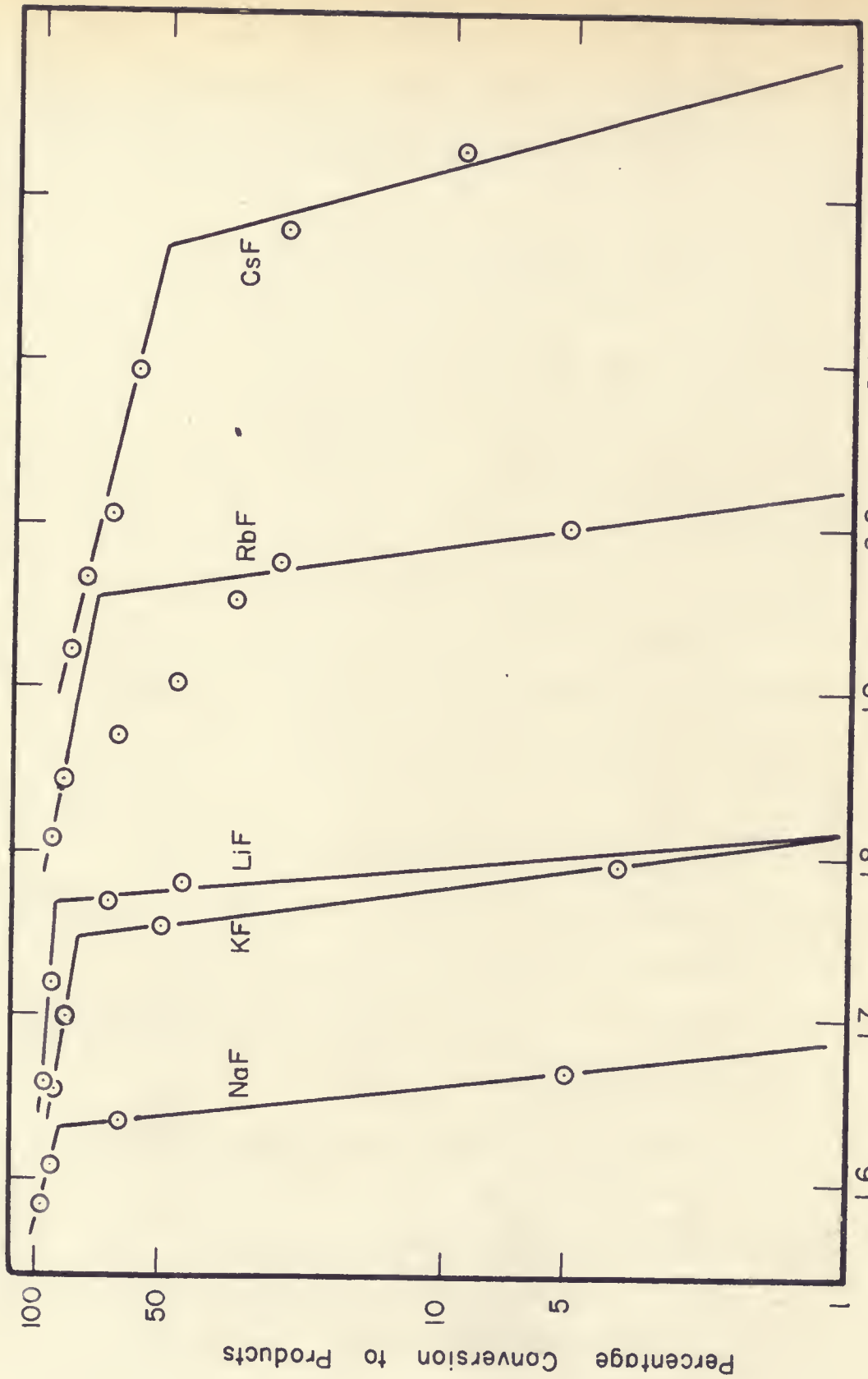


Fig. 11. Percentage Conversion as a Function of Absolute Temperature

TABLE 21

MELTING POINT CORRELATIONS

Salt	LiF	NaF	KF	RbF	CsF	CaF_2	BaF_2
M.P., °K.	1143	1266	1129	1026	957	1628	1552
Temp., 0% Conv., °K. Fig. 10	555	599	556	497	444	620	620
$\frac{\text{T, °K., 0\% Conv.}}{\text{T, °K., M.P.}}$	0.485	0.473	0.493	0.485	0.464	.381	.399
Intersection, Fig. 11, °K.	564	613	572	512	461	—	—
$\frac{\text{T, °K., Intersection}}{\text{T, °K., M.P.}}$	0.493	0.485	0.507	0.499	0.482	—	—

was found to be approximately one-half the absolute melting point of the salt. The melting points listed in this table for the alkali fluorides were taken from those reported by Damiens[56] in a critical survey of published values. This melting point correlation explained why the conversion curves for LiF and KF were so similar. The order of catalytic activity was clearly a function of the melting point of the salt.

The results obtained in this work indicated that the oxidation of $CF_3CF{=}CF_2$ was controlled by various processes occurring within and on the crystal. Possibly the steep portions in Fig. 11 represented processes occurring just below the Tammann temperature. In this region the reaction would be sensitive to structural detail. The less steep portion of the plot occurring at higher temperatures would correspond to oxidation in the region where bulk diffusion in the crystal had become the dominant process. In this range the defect structure would be expected to anneal out and the oxidation process would be more dependent on thermal effects although structural properties of the crystal would still play an important part.

The observation that the catalytic activity of the alkali fluorides was a function of their melting points led to the prediction that CaF_2 and BaF_2 would not show catalytic activity until temperatures approaching one-half their melting points were reached. The Tammann temperature

for CaF_2 is approximately 541° and for BaF_2 approximately 503°. Since complete conversion was obtained over these two surfaces at temperatures considerably below the Tammann point, it was concluded that thermal reaction was responsible for the results noted. Consideration of the results obtained with a Ni surface free of NiF_2 showed that this conclusion was valid. Fig. 12 shows that the same results were obtained over Ni, CaF_2 and BaF_2. Since these materials all gave the same results, it was concluded that the nature of the surface used was not important to the reaction in this temperature range. A clean Ni surface, one free of NiF_2, would not be expected to show catalytic activity for the oxidation of $CF_3CF{=}CF_2$. The prediction of catalytic activity based on melting temperatures is valid when applied to salts whose Tammann point is below the range in which thermal oxidation occurs.

A tentative mechanism, within the scope of present free radical and solid state physics theories, is proposed to explain the results observed in this research. This possible mechanism for the catalytic oxidation of $CF_3CF{=}CF_2$ is discussed in the following paragraphs.

The reaction of fluorine with organic compounds is generally considered to be free radical in type.[57] A chain initiation mechanism for the reaction of fluorine with olefins has been proposed.

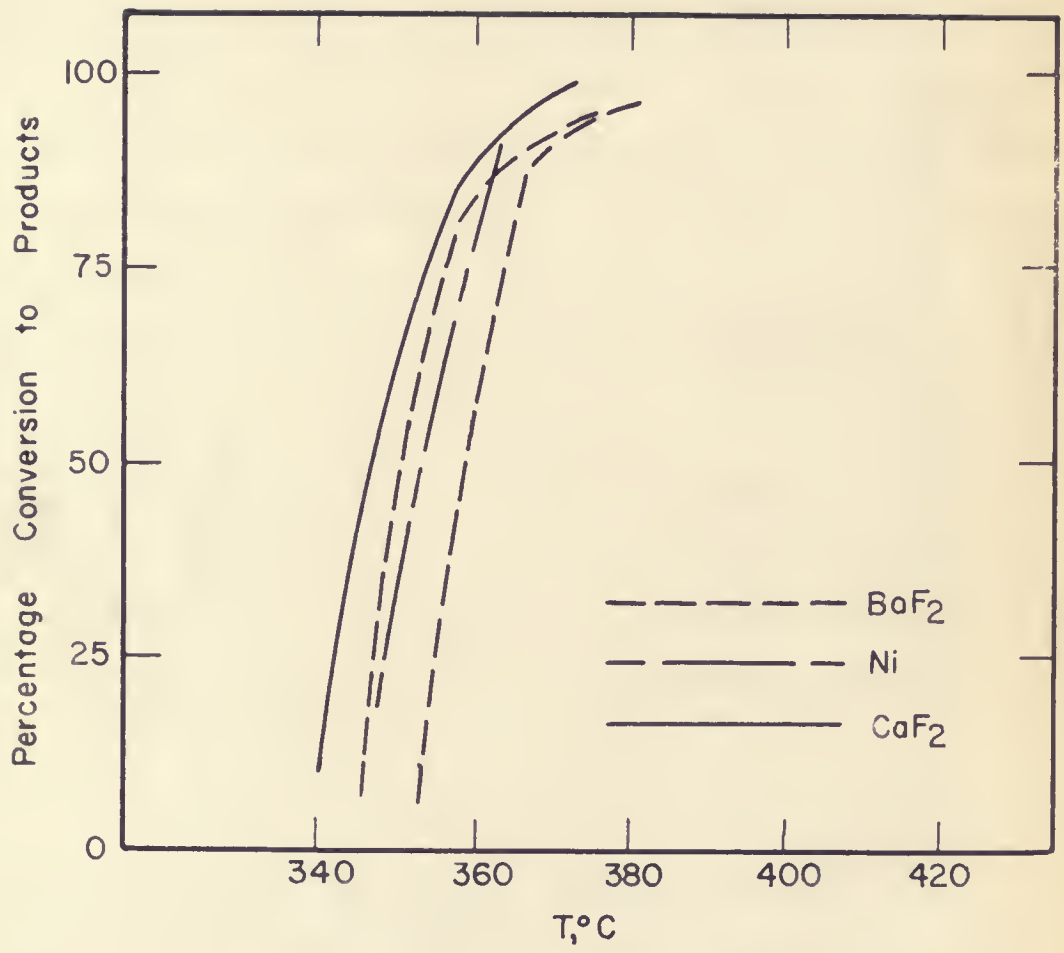


Fig.12. Summary Plot; Percentage Conversion As a Function of T,°C for CaF_2, BaF_2 and Ni

$$-\overset{|}{C}=\overset{|}{C}- + F_2 = -\overset{|}{\underset{F}{C}}-\overset{|}{\underset{\bullet}{C}}- + F\bullet \qquad (15)$$

Miller[58] obtained direct experimental evidence for equation (15) by introducing oxygen into the reaction between fluorine and $CCl_2{=}CCl_2$ at -15° to 0°. Significantly, the formation of the normal and dimer addition products was almost completely inhibited, and a fluorine-sensitized oxidation of $CCl_2{=}CCl_2$ leading to the formation of CCl_2FCOCl, CCl_3COF and $COCl_2$ was observed. These products were formed by the attack of intermediate radicals by oxygen. These oxidation products are closely analogous to those reported in the case of the photochemical chlorine-sensitized oxidation of $CCl_2{=}CCl_2$. There is much evidence to indicate the following chain initiation reaction for this process.[59-61]

$$Cl_2 + h\nu = 2Cl\bullet$$

$$-\overset{|}{C}=\overset{|}{C}- + Cl\bullet = -\overset{|}{\underset{Cl}{C}}-\overset{|}{\underset{\bullet}{C}}-$$

Again the oxidation products were believed to be formed by the attack of oxygen on intermediate radicals.

The role of oxygen in the fluorination of organic compounds has been highly significant because of the difficulty of preparing oxygen-free fluorine.[62] The strong oxidizing effect of oxygen in fluorinations involving the replacement of hydrogen was considered to be due largely to the attack of intermediate radicals by oxygen.[58]

Gens[63] has postulated that fluorine atoms, capable of rapid movement through the crystal, might explain the exchange results observed between fluorocarbons and alkali fluorides. An extension of this idea might explain the results observed in the oxidation of $CF_3CF{=}CF_2$ over alkali fluorides. Activation of the alkali fluoride could conceivably involve the production of free fluorine atoms in the crystal. These radicals would then be capable of attacking the olefin to form intermediate radicals of the type previously discussed. Attack of oxygen on these intermediate radicals could then account for the various products formed using a scheme similar to that proposed by Miller.[64] Attack of fluorine atoms on the olefin double bond would account for the apparent migration of fluorine observed in the products formed. In the simplest case CF_3COCF_3 would form when fluorine atom attack took place on the number one carbon of the olefin. Conversely CF_3CF_2COF would form when fluorine atom attack took place on the number two carbon.

It was noted that the alkali fluoride catalysts used in this work had to be activated by first initiating the reaction at a temperature higher than that required for reaction over the activated crystal. This fact could be connected with the production of V_1 center[65] type defects in the crystal. Once these centers were produced by the initial high temperature reaction, excess fluorine atoms

would then be present in the crystal to initiate the reaction at lower temperatures. This overall process is considered in the following paragraphs.

The primary step in this heterogeneous catalytic reaction must be the attachment of a molecule of $CF_3CF{=}CF_2$ to the catalyst surface. Once adsorbed on the surface the molecule may possibly be dissociated into radicals and atoms, this dissociation depending on thermal energy and on activation energies for the particular system. The ability of a surface to induce dissociation of a molecule is a specific property of the system under consideration and is related to the chemical affinity of the two substances.

Once fluorine atoms are formed in this high temperature process, the simplest way for this excess halogen to diffuse into the crystal would involve a defect process.[66] Vacant cation sites and positive holes could migrate from the surface into the interior. The metal ions and electrons produced in this fashion could then react with the fluorine atoms produced at the surface. The important aspect of this sequence would be the production of free fluorine atoms in the crystal. These would arise from interaction of the cation vacancy with the positive hole. The cation vacancy would trap the positive hole, thus localizing it, and produce a fluorine atom. This electrostatically unencumbered entity would be capable of rapid

migration to the surface where it could initiate the low temperature oxidation reaction.

The important point to consider in this process is that the stoichiometric excess of fluorine atoms which could initiate the low temperature oxidation reaction were initially produced by the high temperature reaction.

This tentative mechanism offers an explanation of why the reaction was not surface area limited. The rate determining step in the reaction could be dependent on the activity of fluorine atoms in the crystal. This could be true since for catalytic reactions it is presumed that the activation energy for reaction is made available at surface defects, which in this case would involve a fluorine atom. Fluorine atom mobility would be dependent on the Tammann temperature for each salt. The difference in mobility of fluorine atoms for the various alkali fluorides was probably sufficient to overshadow other effects such as surface area.

The unique resistance of the saturated fluorocarbon, C_3F_8, to oxidation, is understandable in terms of the mechanism used to explain the ready oxidation of C_3F_6. Saturated fluorocarbons are known to exchange fluorine with alkali fluorides only with difficulty and at much higher temperatures than required for unsaturated fluorocarbons. Fluorine exchange between the saturated compound C_3F_8 and an alkali fluoride appears to involve a different process from that for the unsaturated compound C_3F_6. The small

amount of exchange observed for saturated fluorocarbons at high temperatures is probably a simultaneous exchange between fluorine of the crystal and the adsorbed molecule without production of intermediate radicals. This view is substantiated by the observation that no oxidation products were obtained with C_3F_8 over CsF at temperatures up to 620°. Lack of radical formation would account for the lack of oxidation products under conditions where fluorine exchange was occurring.

An appreciable selectivity in products formed was found between CsF and NaF in the preliminary experiments. The compound, CF_3OCF_2COF, was formed in good yield over NaF at 300°. This product was not isolated from the oxidation products over CsF at 215°. The compound, $CF_3COCF_2CF_3$, was obtained in good yield over CsF but was never isolated in the products from the oxidations over NaF. This difference in products was undoubtedly connected with the difference in lattice parameters for these two fluorides, as well as with the lowered activation energy for the process over CsF. The significance of the two to one ratio of COF_2 to CF_3COF was not understood. This ratio was approximately constant for CsF, NaF as well as NiF_2.

Three compounds, previously unreported, were identified among the reaction products from the oxidation of $CF_3CF{=}CF_2$.

A gem-diol, $CF_3C(OH)_2CF_3$, corresponding to the monohydrate of CF_3COCF_3 was identified. A solid hydrate of CF_3COCF_3 has been reported in the literature although samples pure enough for characterization were never obtained. The solid sample, obtained in this work, melting at 44.5° to 46.0° was believed to be a relatively pure specimen. The high melting point of this material is attributed to its symmetrical structure and the possibility of hydrogen bonding.

The new acid fluoride, CF_3OCF_2COF, does not represent a new class of fluorocarbon acids as acids of the type $CF_3(CF_2)_nOCF_2CF_2COOH$ containing an oxygen linkage have been reported.[67] These acids were prepared by the Simons electrochemical process. It is interesting to note that an attempt to prepare CF_3OCF_2COF, in this laboratory by the electrochemical process was unsuccessful. The major products obtained were CF_4, OF_2 and CF_3OCF_3. This new acid fluoride was of interest to the synthetic chemist since it would facilitate the preparation of new fluorocarbon derivatives containing an oxygen linkage in the carbon skeleton.

A third new compound was found among the oxidation products. This material was tenatively assigned the structure $(CF_3)_2CFCOCF_2CF_3$ on the basis of the hydrolysis products obtained from cleavage with NaOH solution.

The varied and unusual products obtained from the oxidation of a single reactant indicate that this catalytic method should find considerable use for the oxidation of reactive fluorocarbon materials.

A number of piperazine and N-phenylpiperazine derivatives of the commonly available fluorocarbon-acids were prepared. These salts were exceptionally easy to prepare and purify. Their melting points were in a convenient range and were quite reproducible. In view of the many recent developments in the field of fluorine chemistry, it was felt that these derivatives would be of value to other researchers in the identification of acidic materials.

CHAPTER VIII

CONCLUSIONS

This work was undertaken in an attempt to find materials that would be useful as catalysts for reactions of fluorocarbon compounds. The reaction of $CF_3CF{=}CF_2$ with oxygen over a number of different surfaces was studied. The classical oxidation catalysts of organic chemistry, studied in this work, were found to be unsuitable for the oxidation of fluorine containing compounds from the standpoint of useful products. Cupric oxide gave mainly CO_2 as a product. The main reaction occurring over Hopcalite oxidation catalyst was:

$$CF_3CF{=}CF_2 + \text{Metal Oxides} = 3CO_2 + \text{Metal Fluorides.}$$

A number of inorganic fluorides were studied as oxidation catalysts. The alkali fluorides were all found to catalyze the oxidation of $CF_3CF{=}CF_2$. The order of catalytic activity was CsF $>$ RbF $>$ KF, LiF $>$ NaF. This sequence agreed with the order of fluorine exchange observed for $CF_3CF{=}CF_2$ and the alkali fluorides by other workers. The catalytic activity of these salts was shown to be a function of their melting points. The oxidation

process was not a surface area limited process. Although the exact mechanism of this reaction was not understood, it was postulated that rapid migration of fluorine atoms through defect sites in the crystal might be involved.

New and useful compounds were found among the reaction products over CsF and NaF. Of the alkali fluorides, CsF gave the most satisfactory results in terms of products obtained. The ratio of high-boiling products to low-boiling products was appreciably higher for CsF than for NaF. The oxidation of $CF_3CF{=}CF_2$ over CaF_2, BaF_2 and Ni was thermal in nature rather than catalytic. In the case of Ni, which was studied extensively, this thermal reaction gave only low-boiling products.

The discovery that metallic fluorides were effective catalysts for the oxidation of $CF_3CF{=}CF_2$ was a unique find. Prior work in the field of catalysis would not lead one to consider these materials as useful catalysts for oxidation type reactions. This observation again illustrated the danger in extrapolating the findings of organic chemistry to the field of fluorocarbon chemistry. The success obtained with this new method of oxidation suggested that it will be a useful tool for the oxidation of other reactive fluorine-containing compounds.

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BIOGRAPHICAL SKETCH

Warner H. Christie was born in Brooklyn, New York, on October 29, 1929. He was granted the degree of Bachelor of Science in June, 1951, and the Master of Science in September, 1953, at the University of Miami, Coral Gables, Florida. This same month he was admitted to the Graduate School at the University of Florida. As a graduate student at the University of Florida he was employed as a research assistant on a project sponsored by the Office of Naval Research. He is a member of Sigma Xi.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February 1, 1958

C. F. Byers
Dean, College of Arts and Sciences

Dean, Graduate School

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